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TRANSITION METAL NITRITE COMPLEXES

MICHAEL A. HITCHMAN and GRAHAM L. ROWBOTTOM

Chemistry Department, University of Tasmania, G.P.O. Box 252C, Hobart, Tasmania 7001 (Australia)

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CONTENTS

LIGAND ABBREVIATIONS

en	ethane-1,2-diamine
NN′-dimen	*NN′*-dimethyl(ethane-1,2-diamine)
NN-dimen	*NN*-dimethyl(ethane-1,2-diamine)
m-stien	*meso*-1,2-diphenyl(ethane-1,2-diamine)
NN′-dieen	*NN′*-diethyl(ethane-1,2-diamine)
py	pyridine
NNN′N′-tetmen	*NNN′N′*-tetramethyl(ethane-1,2-diamine)
4-mepy	4-methylpyridine
3-mepy	3-methylpyridine
bipy	2,2′-bipyridyl
N-men	*N*-methyl(ethane-1,2-diamine)
N-een	*N*-ethyl(ethane-1,2-diamine)
i-quin	isoquinoline
2-meim	2-methylimidazole
pyr	pyrazole
acac	acetylacetonate
o-cat	*o*-xylylenebis(triphenyl phosphonium)

A. INTRODUCTION

Because of its ability to function as an ambidentate ligand, the nitrite ion has been of interest from the very earliest days of coordination chemistry. Indeed, the isomerism exhibited by the ion $[Co(NH_3)_5(NO_2)]^{2+}$ featured in the great controversy over the very nature of metal complexes which existed at the beginning of the present century. Ironically, it was the chief protagonist of the losing side in this argument, S.M. Jørgensen, who recognized that the essential difference between the isomeric forms of this species lies in the manner of coordination of the nitrite group. Jørgensen noticed [1] that the colour of the pink, unstable form of this ion is similar to that of the corresponding aquo complex, while the stable yellow form has a colour analogous to that of the hexamine cobalt(III) ion, and correctly deduced that this is an example of linkage isomerism, with the nitrite ligand bound to the metal via oxygen in the former complex and via nitrogen in the latter. This conclusion has recently been confirmed unambiguously by X-ray crystallography [2].

The early literature contains a number of references to the existence of simple transition metal nitrites [3]. However, virtually no work has been carried out on these compounds in recent years, and in the absence of firm analytical data or investigations by modern physical techniques, their nature remains obscure. It is possible that many of these substances may prove to be basic salts with complex polymeric structures, and in fact a detailed investigation of the products formed by crystallizing simple transition metal nitrites from aqueous solution could well prove fruitful. There have also been reports of several simple anhydrous transition metal nitrites [4], but in no case are sufficient data available to be certain of the correct formulation of the compound in question. The vast majority of well characterized nitrite complexes fall into one of two groups: polynitrite species of general formula $(\text{cation})_x\text{M}(\text{NO}_2)_y$, where y may take any value from 3 to 6 depending on the nature of the cation and the metal, and mixed-ligand complexes involving either an aromatic or an aliphatic amine. Rather than consider these on an element by element basis, attention will be focused on various aspects of nitrite chemistry as these apply to the whole range of complexes. The compounds formed by the elements zinc, cadmium and mercury have been included in the discussion, as these metals form a range of nitrite complexes which have properties bearing directly on those of the transition elements.

Much of the interest in complexes of the nitrite ion still centres around the ability of this ligand to coordinate to a metal in a variety of different ways. Today, however, the ready availability of a wide range of physical techniques and the possibility of determining molecular structures relatively easily by X-ray methods, has meant that a considerable body of information has been gathered not only on the way in which the ligand is bound to the metal, but also on the factors which apparently influence the method of coordination adopted and the nature of the metal–nitrite bond. With this in mind, the present review sets out to summarize current knowledge of the chemistry of the nitrite ligand in such a way that answers to the following questions may be attempted: (i) In what ways does the nitrite ion function as a ligand? (ii) How may the various coordination types be recognized experimentally? (iii) What factors appear to be important in influencing the method of nitrite coordination? (iv) What is known about the nature of the metal–ligand bonding associated with the different coordination types?

Before considering these points in detail, it is worth summarizing briefly the various methods of coordination available to the nitrite ligand.

B. METHODS OF COORDINATION OF THE NITRITE LIGAND

The nine different ways in which the nitrite ion might be expected to function as a ligand are shown schematically in Fig. 1 (i–ix). Coordination types (i) through (vii) have all been confirmed by X-ray structures on transition metal complexes. Although it has been proposed [5,6] on the basis of spectroscopic evidence that nitrite groups bridging via two oxygen atoms are present in several nickel(II) complexes, it has been pointed out [7] that it is hard, if not impossible, to distinguish between this kind of nitrite bridge and chelation spectroscopically, and X-ray studies have subsequently shown [8,9] that chelating nitrite groups are present in each of the compounds in question which have been studied by this technique. As yet, therefore, no complex is known in which the nitrite ion functions as a bridging ligand via both oxygen atoms. Similarly, a three-coordinate nitrite group [Fig. 1(ix)] has not yet been observed in a transition metal complex, though this type of linkage has recently been characterized in the compounds $Cd(en)(NO_2)_2$ [10] and $K_2Pb(NO_2)_3NO_3 \cdot H_2O$ [11]. Bonding of this kind is also formally present in the compound $K_2Cd[Cd(NO_2)_6]$, in which half of the cadmium ions are coordinated to six nitrite nitrogen atoms, while the other half are surrounded by twelve nitrite oxygen atoms, each nitrite thus being formally three-coordinate [12]. It should be noted that, in principle, the coordination types (viii) and (ix) may each exist in several forms, depending upon which of the oxygen lone-pair electrons are utilized in bond formation.

A brief discussion of the nomenclature applicable to nitrite complexes is appropriate at this point. Conventionally, as a monodentate ligand a nitrogen bound nitrite is termed a "nitro" group, while one bonded via oxygen is called a "nitrito" group. It has generally been assumed that in nitrito complexes the non-bonded oxygen atom is *trans* to the metal [Fig. 1(ii)] rather than *cis* as in (iii). While X-ray structure determinations suggest that

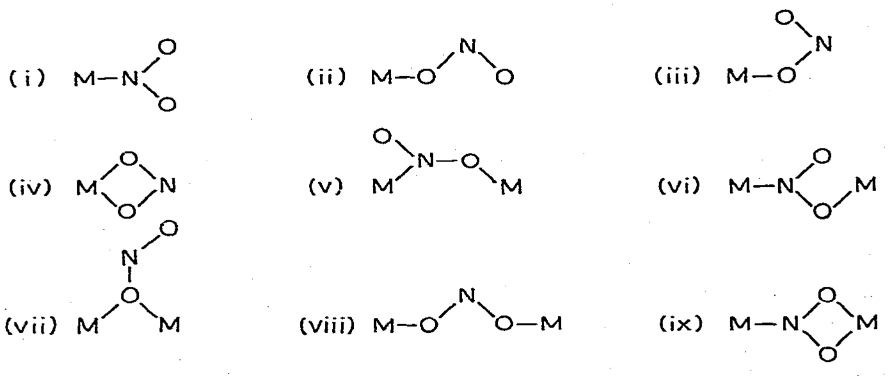


Fig. 1. Possible types of metal–nitrite coordination.

this is usually the case, it is not always so, and it must be remembered that nitrito coordination may in principle be of either kind. Since all types of bidentate nitrite coördination involve at least one oxygen atom, it seems best to follow the convention that all of these are designated as "nitrito" groups, the particular atoms involved being specified in each case. A chelating group is then (*O,O′*-nitrito), a single oxygen bridged group (*μ-O*-nitrito), and a group bridged via nitrogen and oxygen (*μ-N,O*-nitrito). It should be noted that the latter coordination can also take place in two ways, as illustrated in Fig. 1 (v) and (vi). Finally, when the nature of the bonding is to be indicated in a structural formula, this will be done in the present review by italicizing the nitrite atom or atoms coordinated to the metal. Thus, the two forms of the complex ion of stoichiometry $[Co(NH_3)_5(NO_2)]^{2+}$ are indicated by $[Co(NH_3)_5(\mathit{N}O_2)]^{2+}$ and $[Co(NH_3)_5(\mathit{O}NO)]^{2+}$.

Before considering how the various sorts of nitrite coordination may be recognized experimentally, it is worth reviewing briefly the structural characteristics of typical complexes containing each coordination type and also the changes in the internal nitrite geometry which accompany the different modes of bonding. The transition metal nitrite complexes of known crystal stucture are tabulated in an appendix, together with details of the nitrite coordination.

C. GENERAL CLASSIFICATION OF NITRITE COMPLEXES ACCORDING TO COORDINATION TYPE

(i) Nitro coordination

This is a very common type of nitrite coordination, occurring in numerous amine complexes of cobalt(III), platinum(II), palladium(II), ruthenium(III), rhodium(III) and nickel(II), as well as in a wide variety of hexanitrometallates involving Co^{2+}, Co^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Rh^{3+}, Cd^{2+}, La^{3+} and Pt^{4+} and in the tetranitro ions of Pt^{2+} and Pd^{2+} (see appendix). When a complex contains more than one nitro-group, these usually adopt a *trans* configuration. However, this is not invariably the case, as while the nitrite ligands in $[Ni(en)_2(\mathit{N}O_2)_2]$ have a *trans* arrangement [13,14] it has been reported that this complex also crystallizes as a monohydrate, $[Ni(en)_2(\mathit{N}O_2)_2]\cdot H_2O$, in which the nitro groups are *cis* to one another [9,15]. Generally, *trans* nitro groups are found to be coplanar. For instance, numerous hexanitrometallate ions have the geometry illustrated in Fig. 2, while the removal of a pair of *trans* groups from this arrangement produces the geometry observed in $K_2Pt(\mathit{N}O_2)_4$ and $K_2Pd(\mathit{N}O_2)_4$ [16]. However, *trans* nitro groups are not always coplanar, as may be seen from the structure [14] of $[Ni(\mathit{NN'}\text{-dimen})_2(\mathit{N}O_2)_2\cdot H_2O$ illustrated in Fig. 3(a). It is thought

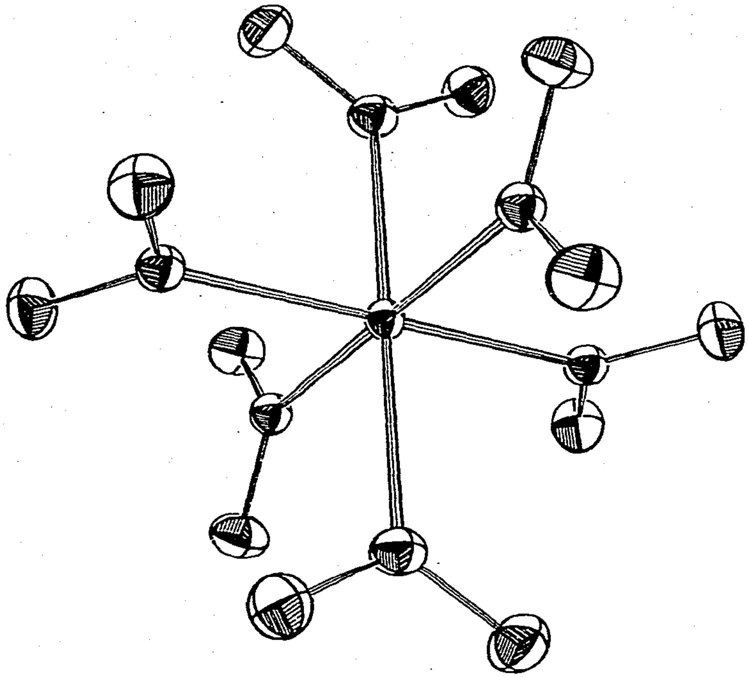


Fig. 2. Geometry observed for many hexanitrometallate ions.

that the interligand repulsions are responsible for the adoption of a staggered arrangement of the nitro groups in this complex (see section F(ii)) [14].

(ii) Monodentate nitrito coordination (non-bonded oxygen trans *to the metal)*

For many years this type of coordination was known only in a number of thermodynamically unstable amine complexes of cobalt(III), platinum(II) and rhodium(III) [see section F(i)]. Recently, however, compounds containing stable linkages of this kind have been prepared for a variety of metal ions. Thus, this type of coordination is thought to be present in a number of chromium(III) amine nitrite complexes on the basis of their IR [17–19] and electronic [17,19] spectra, and this has been confirmed in two cases by crystal structure determinations [20,21]. Again on spectral evidence, Goodgame et al. suggested this type of metal nitrite bonding for various compounds of general formula $M(diamine)_2(NO_2)_2$, M = Ni [22], Co [23] and Zn [24], where diamine is a substituted ethylenediamine, and $M(L)_4(NO_2)_2$, M = Ni [22,25] and Co [23] where L represents an aromatic amine such as pyridine. This has been confirmed by X-ray analysis for the complexes $M(\mathit{NN}\text{-dimen})_2(\mathit{O}NO)_2$, M = Ni [14,26], Co [23] and Zn [27], and

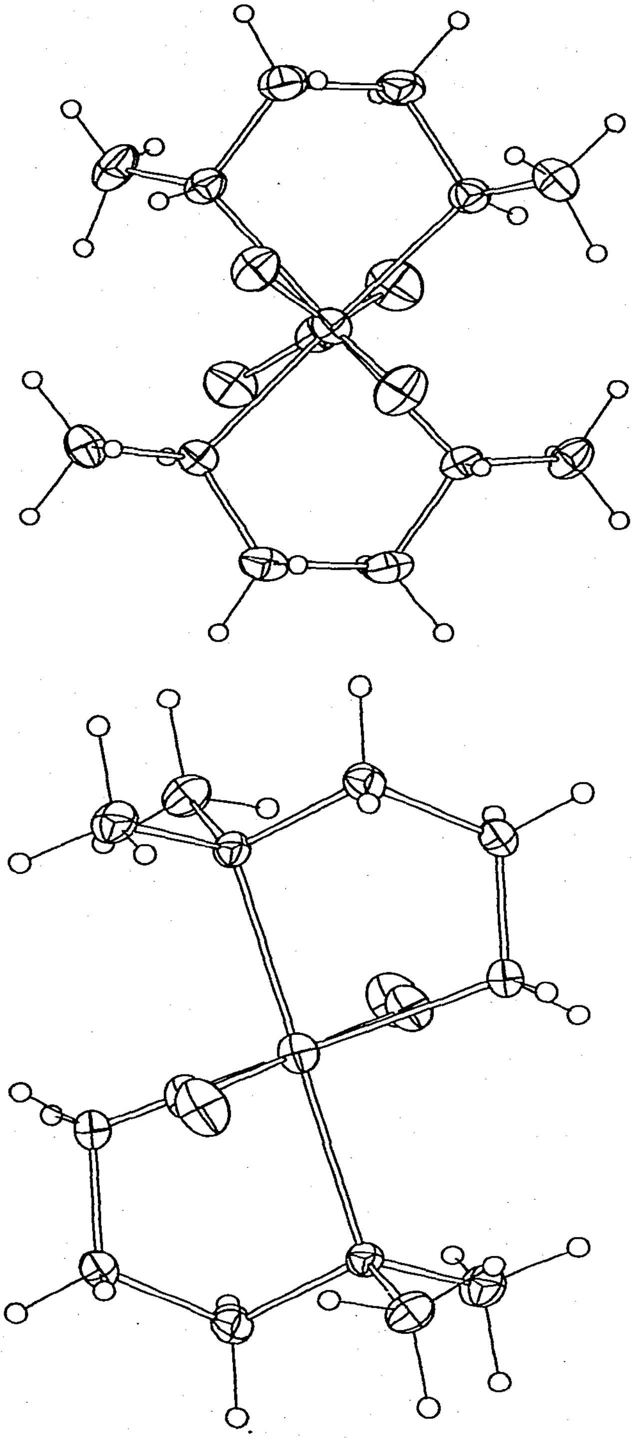
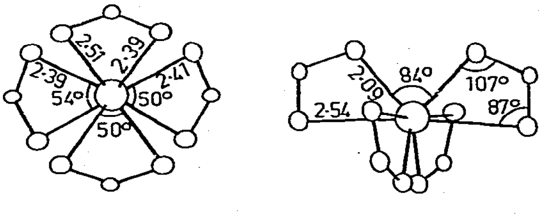


Fig. 3. Geometry of the molecules: (a) Ni(*NN′* dimen)$_2$(*N*O$_2$)$_2$ and (b) Ni(*NN* dimen)$_2$(*O*NO)$_2$ in each case looking down the metal–nitrite bond direction [14].

$NiL_4(\mathit{O}NO)_2$, L = pyridine, 4-methylpyridine and pyrazole [28], and 2-methylimidazole [29]. The structure of Ni(*NN*-dimen)$_2$(ONO)$_2$ is shown in Fig. 3(b). The compounds Ni(*m*-stien)$_2$(NO_2)$_2$ [30] and Ni(*NN'*-dieen)$_2$-(NO_2)$_2$ [31], however, have each been found not to contain monodentate nitrito groups, but to be of the form [Ni(diamine)$_2$(O_2N)]NO_2, containing one chelating and one ionic nitrite ion. El-Sayed and Ragsdale have proposed [32] that a range of compounds of the form Ni(L)$_2$(NO_2)$_2$, contain monodentate nitrito groups, where L is a ligand such as 2-aminomethylpyridine, but, since the IR spectra of the anions are similar to those of the latter two complexes above, this conclusion must remain doubtful.

(iii) Monodentate nitrito coordination (non-bonded oxygen cis *to the metal)*

Nitrito coordination in which the formally non-bonded nitrite oxygen atom is *cis* rather than *trans* to the metal is thought to occur in the tetranitrite ions $M(NO_2)_4^{2-}$, M = Co [33], Cu [33], Zn [45], as well as for some of the nitrite groups in $Cu(NO_2)_5^{3-}$ [34]. The anions in several complexes of the type Cu(diamine)(NO_2)$_2$ are also bound in this way [35–37] and it seems likely that this manner of coordination may well also be adopted in Zn(py)$_2$(NO_2)$_2$ and related compounds [24,38] [see section E(i)]. The geometries observed for the $Zn(NO_2)_4^{2-}$ ion [45] and the molecule Cu(*NNN'N'*-tetmen)(NO_2)$_2$ [36] are shown in Figs. 4(b) and 5. An important feature in which this type of coordination differs from that described in the preceding paragraph is the comparatively close contact between the metal and the second nitrite oxygen atom. This distance is similar to those observed for the longer bonds in numerous tetragonally distorted six-coordinated copper(II) complexes and it seems likely that these "semi-coordinated" ligand atoms make a significant contribution to the total bond energy in compounds of this sort. In fact, nitrito coordination of this kind may also be viewed as a highly asymmetric form of chelation (see following section). An idealized monodentate coordination of this type, in which the



(a) (b)

Fig. 4. Geometry of the tetranitrite ions: (a) $Cd(\mathit{N}O_2)_4^{2-}$ and (b) $Zn(NO_2)_4^{2-}$ [45].

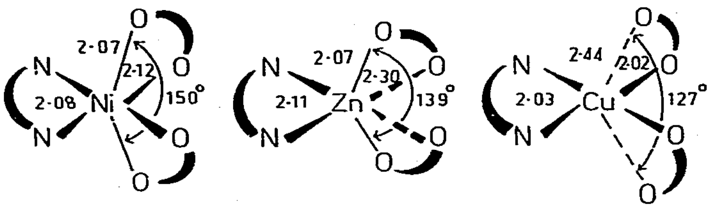


Fig. 5. Diagram showing the coordination geometry about the metal in the isomorphous series M(*NNN'N'* tetmen)$(NO_2)_2$, M=Ni, Zn and Cu.

metal–oxygen bond length is 2.1 Å and the angle MON = 120°, would produce a separation of ~2.95 Å between the second oxygen and the metal. This corresponds to a ratio of the longer to the shorter M–O bond length of $R(MO) = 1.4$. Coordination of this type is observed in one of the $Cu(NO_2)_5^{3-}$ ions present in $K_3Cu(NO_2)_5$ [39]. In practice, however, the above angle is usually greatly reduced from this value, bringing the second oxygen atom much closer to the metal, and an almost continuous range of geometries is observed between symmetrical chelation and the highly distorted groups present [36] in Cu(*NNN'N'*-tetmen)$(NO_2)_2$ (Fig. 5). Following the above arguments, when the ratio $R(MO) > 1.2$ in this kind of coordination the bonding may be considered to be a distorted monodentate arrangement, while when $1.2 > R(MO) > 1$ the bonding may be taken to be an asymmetric form of chelation. It must be remembered, however, that this distinction is essentially one of semantics rather than an abrupt change in bond type.

(iv) Chelation

Although characterized only comparatively recently, it would seem that chelation is a rather common form of nitrite coordination as far as divalent metal ions are concerned. In particular, a wide range of complexes of general formula $[M(diamine)_2(NO_2)]X$ and $[M'(diamine)(NO_2)_2]$ have been found to contain nitrite groups bound in this manner, where M = Ni [9,30,40] or Zn [27,38], and M' = Ni [38,41,42], Co [23] or Zn [24,38], X being a non-coordinated anion such as ClO_4^-, NO_3^- or Cl^-. Indeed, it has recently been discovered that several complexes of the type $Ni(diamine)_2(NO_2)_2$ previously thought to contain monodentate nitrito groups [22] in fact contain one chelating and one non-bonded ionic nitrite [30,31]. The structure of the ion $[Ni(m\text{-stien})_2(NO_2)]^+$ [30] is shown in Fig. 6. Chelating anions are also present in a number of monomeric complexes of Ni^{2+} [42], Co^{2+} [23] and Zn^{2+} [24] of the type $[M(L)_2(NO_2)_2]$ where L is an aromatic amine, as well as in the dimer $[Ni_2(4\text{-mepy})_4(NO_2)_4]\cdot 2C_6H_6$ [43] and the trimer $[Ni_3(3\text{-mepy})_6(NO_2)_6]\cdot C_6H_6$ [43,44], though in the latter two compounds (*N,O*) and *O*-nitrito bridging groups are also present (see Fig. 7). The tetranitrite

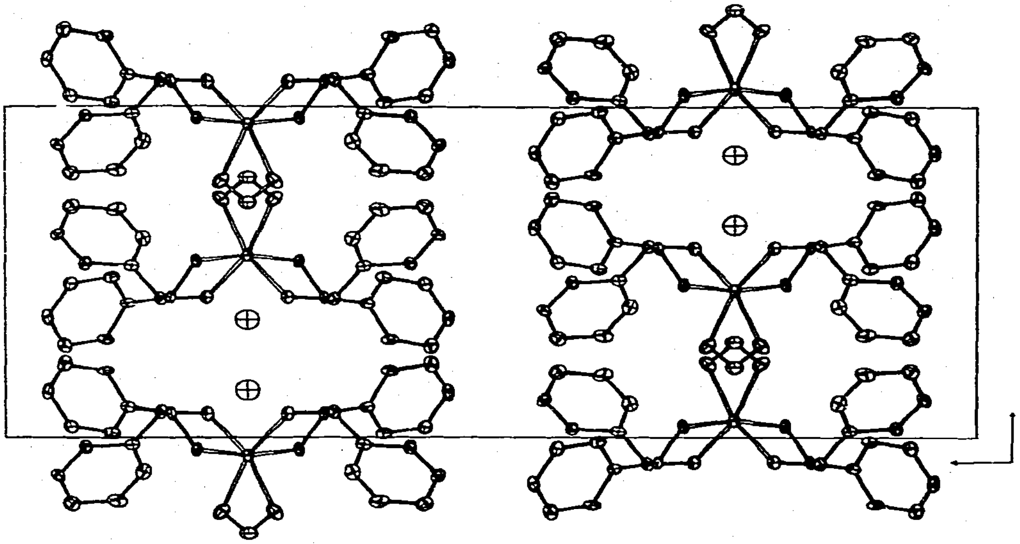


Fig. 6. Unit cell of [Ni(*m*-stien)$_2$(*O*$_2$N)]Cl viewed down the [100] direction [30].

ions $M(NO_2)_4^{2-}$, M = Mn [33], Cd [33,45], Hg [33,46] all contain chelating nitrites while it has been postulated that the pentanitrite ions of Ni^{2+} and Mn^{2+} probably contain both chelating nitrites and nitro groups [7]. Two different kinds of $Cu(NO_2)_5^{3-}$ units are present in $K_3Cu(NO_2)_5$ [34], one containing two chelating nitrites and three nitro groups, and the other two nitro groups and three type (iii) nitrito groups.

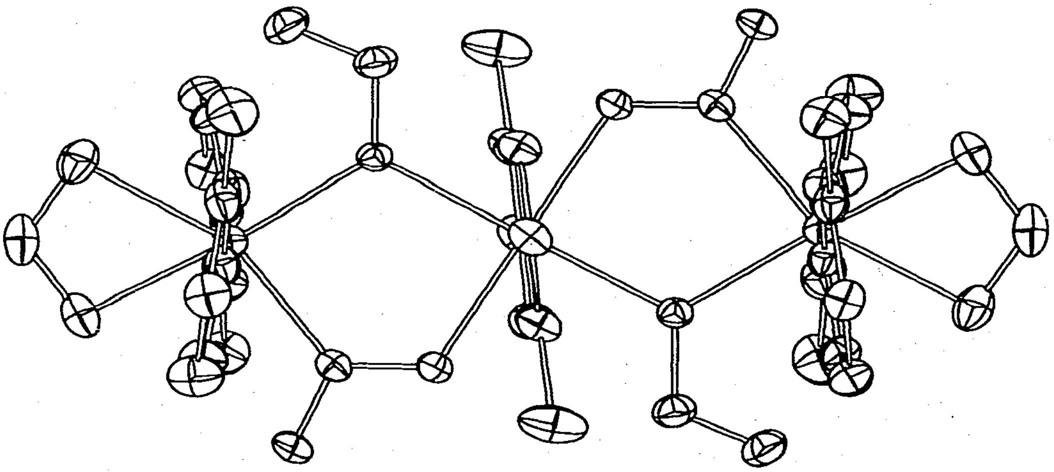
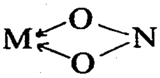


Fig. 7. Geometry of the trimer [Ni(3-mepy)$_2$(NO$_2$)$_2$]$_3$ showing the plane containing the nitrite ligands [43].

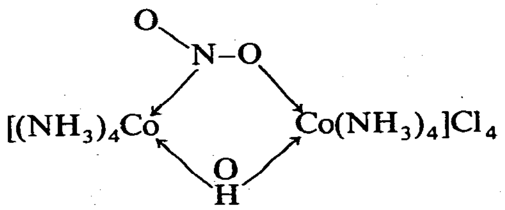
The structure of the $Cd(NO_2)_4^{2-}$ ion [45] is shown in Fig. 4(a), the cadmium(II) ion being surrounded by eight oxygen atoms at the corners of an elongated cube. The $Hg(NO_2)_4^{2-}$ ion has a quite similar geometry [46]. An important feature of the stereochemistry of the chelating nitrite group is the small size of the angle subtended by the oxygen atoms at the metal, which ranges from ~50° for the large Hg^{2+} and Cd^{2+} ions up to ~59° for the Ni^{2+} ion. This raises the question of whether a group of this kind is better thought of as a bidentate ligand, or a single entity occupying just one stereochemical site in the coordination sphere of the metal. If the latter approach is adopted, it is noteworthy that the vectors from the metal to the nitrite nitrogen atoms conform quite closely to a tetrahedral geometry in $Cd(NO_2)_4^{2-}$ [45] and $Hg(NO_2)_4^{2-}$ [46]. The geometries of ions of the type $[M(diamine)_2(NO_2)]^+$, M = Ni [30,31,38,40] and Zn [27,38] are of some interest in this context. In $[Zn(en)_2(O_2N)]^+$ [27] the angle NZnN subtended by the nitrogen atoms *trans* to the nitrite oxygen atoms is ~ 106°, approximately midway between the 90° required by an octahedral stereochemistry and the 120° which would occur in the regular trigonal bipyramidal geometry expected if the metal were effectively five-coordinate. A very similar geometry is observed in the nickel salts containing an ion of this kind [30,31,40], except that the corresponding angle NNiN is ~ 102°, suggesting that here the geometry is significantly closer to an octahedral arrangement. As already mentioned, it is unusual for the two oxygen atoms of a chelating nitrite to be equidistant from the metal ion and it seems clear that the



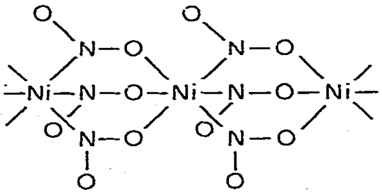
grouping is comparatively "soft" to in-plane distortions, as may be seen from the range of bond lengths exhibited by the complexes illustrated in Figs. 4–6.

(v) μ(N, O) *Nitrito bridging (non-bonded oxygen directed away from both metal ions)*

This is apparently the commonest type of nitrite bridge, having been characterized in a number of dimeric cobalt(III) amine complexes, such as



[47,48], as well as in the polymeric compounds $[Cu_2(bipy)_2(OCH_3)(NO_2)_3]$ [49], $[Ni_2(4\text{-mepy})_4(NO_2)_4] \cdot 2\,C_6H_6$ [43] and $[Ni_3(3\text{-mepy})_6(NO_2)_6] \cdot C_6H_6$ [43,44]. In the copper(II) complex two type (iii) nitrito groups are present in addition to bridging nitrite and methoxy groups, while the nickel(II) complexes contain novel oligomeric structures involving (*N*,*O*) and (*O*) bridging nitrite groups, the terminal positions in each polymer being occupied by chelating nitrite ions. The structure of the molecule $[Ni_3(3\text{-mepy})_6(NO_2)_6]$ [43] is shown in Fig. 7. It is thought that the compound $N(CH_3)_4[Ni(NO_2)_3]$ also contains type (v) nitrite bridges [7]. Although a detailed X-ray analysis of the complex has not been carried out it has very similar unit cell parameters to the analogous chloro and bromo complexes [50] implying that the structure probably consists of linear chains of the form



A particularly interesting series of compounds having structures based upon this type of linkage are the pentameric molecules of general formula $[Ni_5(\text{diamine})_4(NO_2)_8(OH)_2]$ where diamine = en, men, een, *NN'*-dieen, *NN'*-dimen and *NN*-dimen [51]. The structure of the ethylenediamine complex is shown in Fig. 8. The pentamer is centrosymmetric, so that the five nickel(II) ions are rigorously coplanar. The central metal is bridged to each pair of outer nickel(II) ions by a hydroxide group and two nitrite groups. Each pair of outer metal ions are also joined by two nitrite bridges, with the remaining coordination sites, which are directed away from the centre of the oligomer, being taken up by the four diamine groups. Because of the inherent asymmetry of a nitrite bridging group of this kind, its presence in an oligomer always gives rise to the possibility that the metal ion may be present in two or more ligand environments [two "different" nickel(II) ions are present, for instance, in the trimer shown in Fig. 7]. In the pentamer formed by ethylenediamine the disposition of the nitrite bridges is such that three different kinds of nickel(II) are present. The central metal is surrounded by six oxygen atoms, while two of the outer nickels are bound to three nitrogen atoms and three oxygen atoms, and the other two to five nitrogen atoms and one oxygen atom. The corresponding complexes formed by *NN'*-dieen and *NN*-dimen have structures built upon the same basic pentameric geometry, but with subtle differences in the arrangement of the nitrite bridges and, in the case of the asymmetrically substituted diamine, with one of the type (v) (*NO*) nitrito bridges joining each outer pair of nickel(II) ions being replaced by a single oxygen type (vii) nitrito bridge. This change in the coordination of the

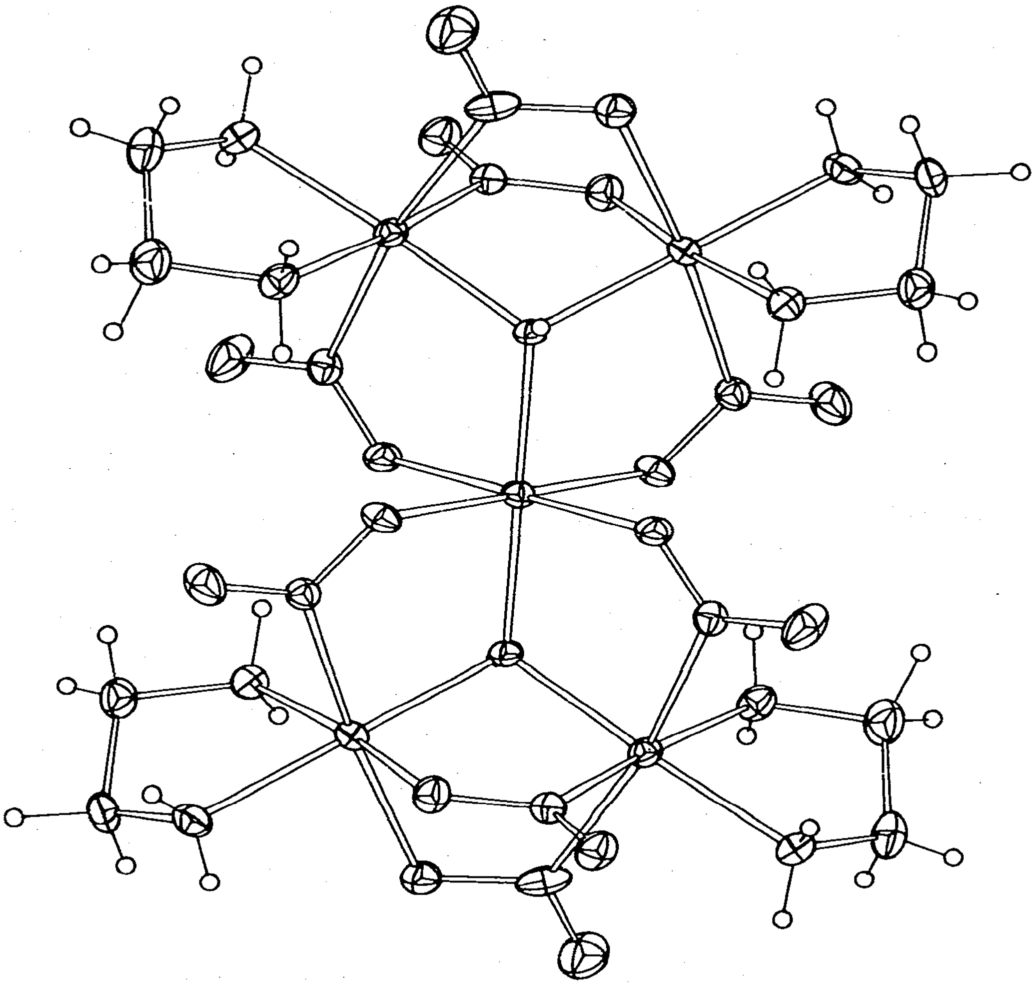
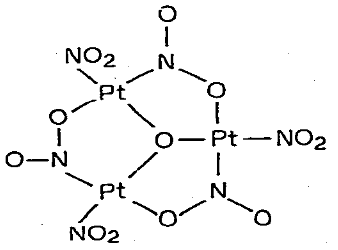


Fig. 8. Geometry of the pentamers [$Ni_5(en)_4(NO_2)_8(OH)_2$] [51].

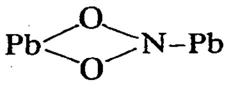
nitrite groups, which produces a marked difference in the electronic spectra of the compounds, is apparently related to the differing steric constraints imposed by the amine substituents [see section F(ii)]. On the basis of spectroscopic evidence, a rather similar kind of structure has been proposed [105] for the compound $K_2Pt_3(NO_2)_6O \cdot \frac{1}{3}H_2O$, with three platinum ions linked via a three-coordinate oxygen ion and (*NO*) nitrito bridges



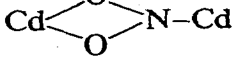
Also on the basis of spectroscopic properties it has been suggested [52] that the complexes Ni(diamine)$(NO_2)_2$, diamine = en, *N*-men and *NN*-dieen, contain nitrite groups bridged via nitrogen and oxygen, though the details of the bridging, and whether this is of type (v) or of the type (vi) discussed below remain unknown.

(vi) μ(N, O) *Nitrito bridging (non-bonded oxygen adjacent to one metal ion)*

Nitrito bridges of this kind, in which the oxygen coordination corresponds to the "*cis*" type (iii) monodentate nitrito linkage discussed above, are comparatively rare, having so far been observed in only two compounds, $Co(NO)_2(NO_2)$ [55] and $[Ni(en)_2(NO_2)]X$, X = ClO_4 [38] or BF_4 [53]. Originally, it was claimed that the latter pair of isomorphous compounds involve a type (vii) *O*-bridged group, with the nitrite being linear [54]. However, this has since been shown to be incorrect, and the structure is as shown in Fig. 9, with linear chains of nickel(II) ions being linked by type (vi) nitrito bridges. The nitrito groups are disordered (a comparatively common feature of nitrite crystal chemistry), either in a completely random fashion or, more probably, on a chain by chain basis. The strict linearity of the chains of metal ions leads to significant deviations of the nickel–nitrite bond directions from idealized octahedral symmetry; in particular, the angle NNiO involving the coordinated nitrite atoms (157°) departs significantly from the 180° required by a regular octahedral arrangement. The bond distances from the metal to the nitrite ligand atoms are also abnormally long in this complex. In contrast to the *cis* monodentate nitrito coordination, in which the nitrite ligand is almost always tilted from an idealized geometry so as to bring the second nitrite oxygen atom closer to the metal, the nitrite bridges in the $[Ni(en)_2(NO_2)]^+$ units are tilted in the opposite sense, the non-bonded oxygen being ~ 3.1 Å from the nickel(II) ion [38]. It may be noted that the limiting situation to result from a rotation of this type of nitrite bridge in a manner that decreases the second metal–oxygen interaction, is the symmetrical tridentate nitrite coordination illustrated in Fig. 1(ix). In fact, it seems likely that any coordination geometry between an essentially bidentate nitrito bridging arrangement, and a symmetrical tridentate grouping should be possible, and, while the two M–O distances of the



group in $K_2Pb(NO_2)_3(NO_3)$ are almost equal (2.69 and 2.77 Å) [11] the analogous bond lengths of the



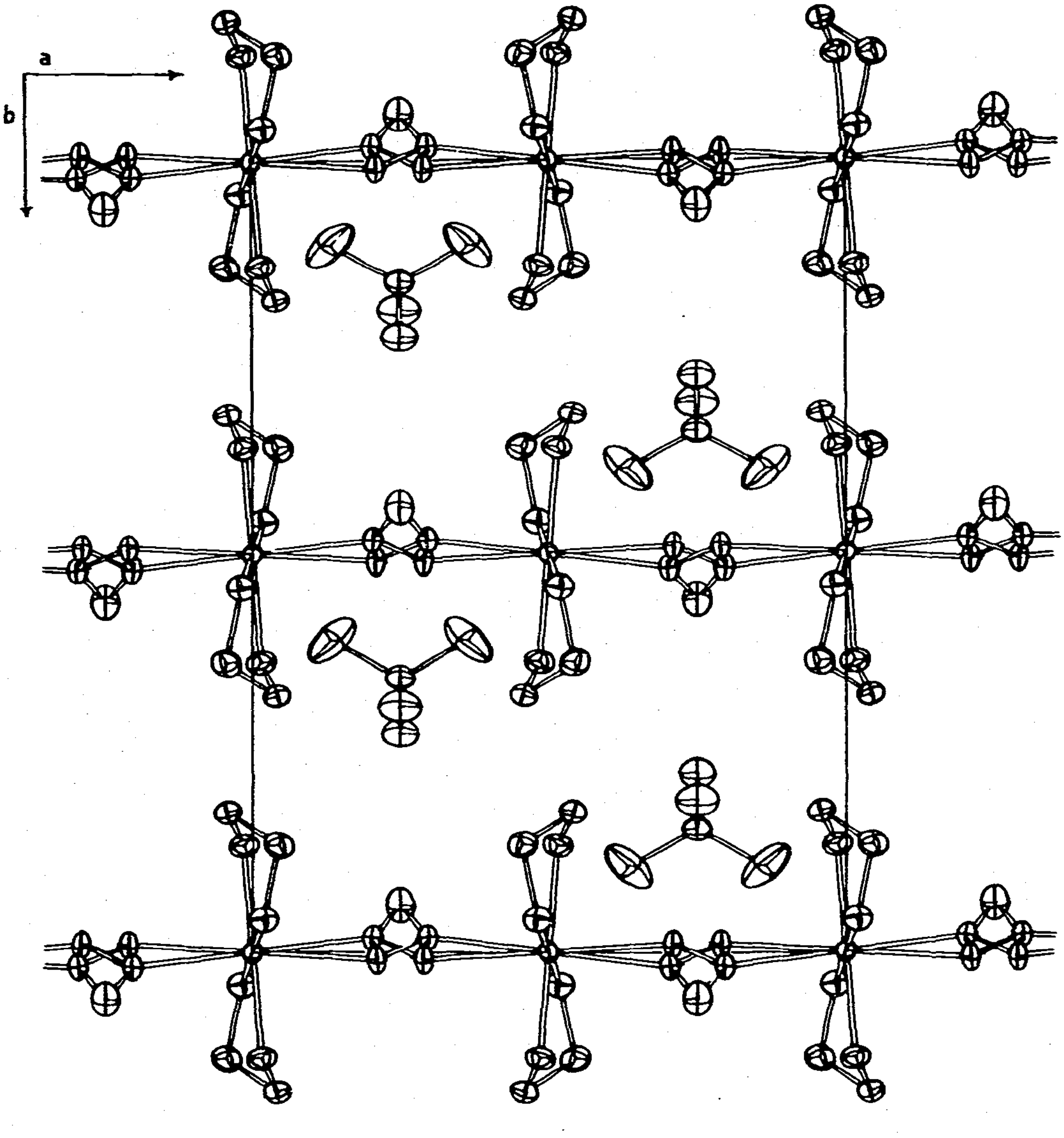
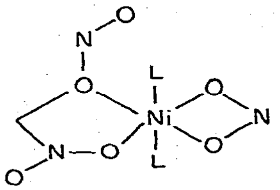


Fig. 9. Unit cell of the compound $[Ni(en)_2(NO_2)]ClO_4$ viewed down the [001] direction. Note that the bridging nitrite groups are disordered [38].

linkages in $Cd(en)(NO_2)_2$ differ quite significantly (2.13 and 2.42 Å) [10]. This may well reflect the difference in size of the Cd^{2+} and Pb^{2+} ions, the latter metal being able to accommodate seven equivalent ligands in its coordination sphere more easily than the former. The fact that the nitrite is tilted in the opposite sense in the nickel(II) complex may be rationalized by the strong tendency of this metal ion to adopt a coordination number of 6 rather than 7.

(vii) μ(O) Nitrito bridging

Apart from the tetrameric molecule $Co_4(NO)_8(NO_2)_2(N_2O_2)$, which contains a quadridentate hyponitrite linking four cobalt(II) ions, in addition to two *O*-bridged nitrito groups [56], this type of nitrite coordination is known only in two types of polymeric nickel(II) complex. The pentameric molecule $[Ni_5(NN\text{-dimen})_4(NO_2)_8(OH)_2] \cdot CH_3CN$ contains two such groups per formula unit, in conjunction with six type (v) (*N,O*) nitrito bridges and two bridging hydroxide ions [51] [see section F(ii) for a more detailed discussion of the geometry of these compounds]. It has also been postulated [52] that single oxygen-bridged nitrite groups occur in a series of complexes of stoichiometry $NiL_2(NO_2)_2 \cdot xC_6H_6$ where L is pyridine, 3-methylpyridine, 4-methylpyridine and i-quinoline. The first three compounds contain 1/3, 1/3 and 1 molecule of benzene per nickel ion, and the novel structure of the 3-methylpyridine complex [43,53] is shown in Fig. 7. The central nickel of the linear, centrosymmetric trimer is bridged to each outer nickel by one (*O*)-bridged and one type (v) (*N,O*)-bridged nitrite. The terminal coordination sites of the polymer are occupied by two chelating nitrite ions, with the six amine groups bonding above and below the plane defined by the metal ions and the nitrite groups. The 3-methylpyridine complex adopts a somewhat similar geometry except that one of the outer units:



is replaced by a chelating nitrite ion, leading in this case to a dimeric, rather than a trimeric structure. Both polymers clathrate benzene, this being apparently necessary in order to stabilize each crystal structure. The angle NiONi subtended by the *O*-bridged nitrite is ~ 120° in both polymers, and a similar value is observed in $Co_4(NO)_8(NO_2)_2(N_2O_2)$, implying that essentially sp^2 hybrid lone-pair orbitals are utilized by the bridging nitrite group in each case.

D. EFFECT OF LIGATION ON THE INTERNAL NITRITE GEOMETRY

It is of interest to consider how the geometry of the nitrite ion is perturbed when it coordinates to a metal in the various ways described above. The structure of the free ion may be taken as that observed in $NaNO_2$

TABLE 1

Average geometry observed for the nitrite ion coordinated in different ways. See Appendix for details of the structures included in the analysis

Metal	Coordination type	No. of nitrite groups	Average nitrite NO bond lengths (Å) [a]	Bond angle (°)
Na	Ionic	1	1.240(3) [b]	114.9(5) [b]
Co(III)	Nitro	43	1.219(29)	119.1(27)
Ni(II)	Nitro	8	1.240(8)	116.8(4)
Cu(II)	Nitro	14	1.245(8)	116.6(8)
Ni(II)	Chelating	9	1.257(7)	112.5(11)
Cu(II)	Chelating	6	1.231(50)	113.0(20)
Zn(II)	Chelating	4	1.245(10)	112.9(12)
M(III)	Type (ii) *O* nitrito	3	1.313(23), 1.207(67)	112.5(5)
M(II)	Type (ii) *O* nitrito	3	1.285(19), 1.177(37)	114.3(10)
Ni(II)	Type (vii) *O* bridging	1	1.305(4) [b], 1.197(4) [b]	114.4(2) [b]
Ni(II)	Type (v) (*NO*) bridging	5	1.285(35), 1.215(23)	115.0(11)
Co(III)	Type (v) (*NO*) bridging	1	1.307 [c], 1.227 [c]	113.7 [c]
CH_3NO_2	Nitro [d]	–	1.224(5)	125.5(5)
cis-CH_3ONO	Nitrito [e]	–	1.398(5), 1.182(5)	114.8(5)
trans-CH_3ONO	Nitrito [e]	–	1.415(5), 1.164(5)	111.8(5)

The following criteria were applied for inclusion: (i) *R* factor < 10%; (ii) standard deviation of metal–ligand bond lengths <0.01 Å; (iii) standard deviation of nitrite NO bond lengths <0.02 Å; (iv) no disorder present among the nitrite atoms; (v) reasonable thermal parameters for the nitrite atoms; (vi) sufficient data reported to allow the application of these criteria.

[a] For the coordination types in which the nitrite oxygen atoms are inequivalent, the bond length to the oxygen coordinated to the metal is given first. The standard deviation is given in parentheses. [b] Note that the standard deviation in this case refers to that reported for a single structure. [c] No standard deviation reported. [d] Data from ref. 264. [e] Data from ref. 60.

[57] (a similar geometry has been observed in other compounds containing ionic nitrite ions [58,59]). The geometries of the nitrite groups in those complexes studied up to the present by X-ray crystallography are listed in the Appendix, together with the type of coordination. The average N–O distances, and the ONO angle, determined statistically for those complexes where the nitrite groups are defined accurately and reliably are listed for each method of coordination in Table 1. In order to make the comparison more meaningful, the complexes have been subdivided where possible according to the nature and oxidation state of the metal; relevant parameters for the limiting covalent compounds CH_3-NO_2 and the two forms of CH_3ONO have also been included. For both chelation and nitro coordination the average of the two N–O bond lengths observed in each structure has been used.

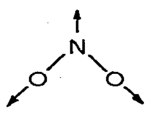
It is apparent that nitro coordination has little effect on the nitrite N–O bond length, this possibly shortening marginally. However, this mode of bonding does cause a significant opening of the ONO angle, by about 2° on coordination to a divalent metal ion, 4° on coordination to cobalt(III), and 10.6° on going from ionic nitrite to nitromethane. Chelation also has no detectable effect on the N–O bond length, but produces a slight but significant decrease of ~2° in the ONO angle. Monodentate nitrito coordination, on the other hand, does not alter the ONO angle, but produces a sizable inequality (0.107 Å) in the N–O bond lengths, these diverging from the free-ion value by about half the amount observed in the limiting covalent compound, methylnitrite. As expected, the bond involving the oxygen coordinated to the metal is that which lengthens. Bridging of the nitrite between two nickel(II) ions via a single oxygen atom has a very similar effect. Bridging via a nitrogen and an oxygen atom also causes the bond involving the coordinated atoms to lengthen, the second N–O bond shortening, though the effect is less pronounced than when coordination takes place solely via a nitrite oxygen atom. Both monodentate and bridging nitrito groups are often disordered in the solid state and except where noted otherwise, data from such groups have been excluded from Table 1. In this context it should be noted that the molecular parameters observed for disordered nitrite groups generally do not parallel those observed when no disorder is present, the N–O bond length involving the uncoordinated nitrite oxygen atom being often significantly longer than that to the coordinated oxygen [2,28,43]. Since this disagrees both with the results obtained from complexes where no disorder is present, and with simple theories of chemical bonding, we think that the geometries estimated for the disordered groups are probably not realistic.

E. INVESTIGATION OF METAL NITRITE COMPLEXES BY PHYSICAL TECHNIQUES

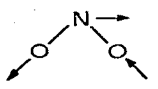
The linkage isomerism present in various cobalt(III) nitrite complexes was first recognised some eighty years ago using that extremely sensitive tool, the human eye, and this can still provide a useful guide to the type of coordination occurring in the nitrite complexes of certain metal ions. For instance, nickel(II) complexes containing nitrite groups bound to the metal via nitrogen, whether as monodentate nitro groups or (*NO*) bridges, are red or yellow, while those in which oxygen-coordinated groups are present are blue or green. When nickel(II) ions in both environments occur simultaneously, the resulting solid or solution is black or dark purple. In recent years, an ever increasing battery of sophisticated physical techniques has become available, which may be used to provide information both on the manner of nitrite coordination and the nature of the metal–nitrite bond. Of these, by far the most widely used have been IR and electronic spectroscopy, supplemented by an increasing number of X-ray crystal structure determinations. However, it is to be expected that other techniques, particularly nitrogen and oxygen NMR, and Raman spectroscopy will become increasingly important in the future. A summary of the most important results obtained using the various methods is given below.

(i) IR spectroscopy

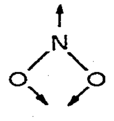
The free nitrite ion belongs to the pointgroup C_{2v} and exhibits the three fundamental modes illustrated below, each of these being both IR and Raman active. The vibrational spectra of several ionic nitrites have been extensively studied in the solid state and solution by various groups [61–65].



ν_s



ν_{as}



δ_{NO_2}

The IR spectrum of $NaNO_2$ is shown in Fig. 10, from which it may be seen that ν_{as} occurs as a broad intense peak centred at ~ 1260 cm^{-1} with ν_s being barely visible as a weak absorption at 1330 cm^{-1} and δ_{NO_2} occurring as a sharp peak at 828 cm^{-1}. The Raman spectrum of the nitrite ion shows peaks at similar energies, but with the relative intensities of ν_{as} and ν_s reversed [61,62,65]. As yet, few studies of the Raman spectra of metal nitrite complexes have been made, but the reversal in the relative intensities of ν_{as} and ν_s should in future make this a powerful method of identifying the nitrite vibrational modes in a complex, since it is often difficult to identify the comparatively weak symmetrical NO stretching peak by IR spectroscopy. It may be noted that NO_2^- is unusual in that ν_s occurs at higher energy than ν_{as}, a feature which is also observed for the isoelectronic molecule O_3 [66] and for OF_2 [67]. This has been explained as being due to the relatively high interaction force constant between the terminal atoms in these three species [63]. Unfortunately, despite the unequivocal evidence provided by the IR and Raman studies, coupled with that from an analysis of the fluorescence spectrum of $NaNO_2$ [64] several papers [22,42,69,70] concerned primarily with the IR spectra of coordinated nitrite groups have incorrectly reversed the assignments of ν_s and ν_{as}, apparently on the grounds that an antisymmetric stretch must always be higher in energy than a symmetric one. However, this is not always the case, and there can be little doubt that the above assignment is the correct one.

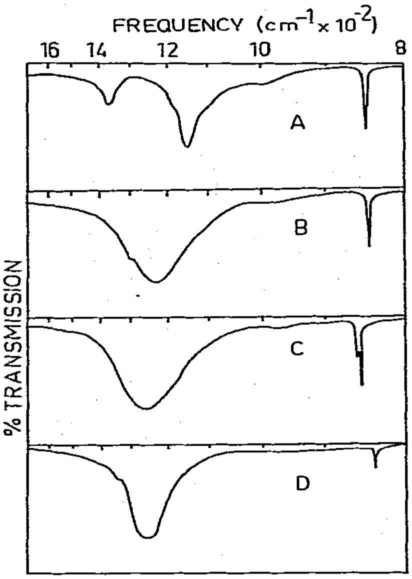


Fig. 10. IR spectra of some tetranitrite complexes [182]: $Cs_2Zn(NO_2)_4$ (A), $Cs_2Mn(NO_2)_4$ (B) and $K_2Cd(NO_2)_4$ (C). The spectrum of $NaNO_2$ (D) is shown for comparison.

Upon coordination to a metal, the stretching frequencies of the nitrite change in a manner which is generally quite characteristic of the type of bond which is formed, making vibrational spectroscopy a powerful method of deducing the mode of nitrite coordination in a complex. However, it should be borne in mind that hydrogen bonding to the nitrite atoms not coordinated to the metal may also produce significant shifts in the vibrational frequencies, so that particular caution should be exercised in drawing conclusions about the nitrite coordination from IR spectra when molecules with the potential to hydrogen bond are present in a solid. It has also been observed [106,107] that traces of NO_3^- impurity may give rise to peaks in the region ~ 1400 cm^{-1} and 830 cm^{-1} which may be incorrectly assigned to coordinated nitrite groups.

The spectral characteristics of each type of nitrite coordination are discussed individually below.

(a) Nitro coordination

The IR spectra of the nitro complexes of numerous metal ions have been reported. In particular, the spectra of the hexanitrometallates of Co(III) [71–76], Ni(II) [7,71,77,78], Cu(II) [77,78], and Co(II) [77,78] have been studied extensively, and representative peak energies are listed in Table 2. A discrepancy exists in the literature concerning the peaks due to ν_{as} for the ions $M(NO_2)_6^{4-}$, M = Co, Ni and Cu, these being reported in the range 1280–1380 cm^{-1} by Nakagawa et al. [71], Goodgame and Hitchman [7], Brooker and Irish [107], and LePostollec et al. [78], but ~ 1650 cm^{-1} by Elliot et al. [77]. These last spectra are considered to be in error. The reason for this is not clear, though it has been suggested that the anomalous peaks could be due to trace amounts of water [107]. A normal coordinate analysis has been made of the ions $Co(NO_2)_6^{3-}$ and $Ni(NO_2)_6^{4-}$ and the influence of the lattice symmetry on the spectra was reported [71]. Several studies of the IR spectra of the nitro complexes formed by cobalt(III) [70,74,79–87] and nickel(II) [24,88,89] with a variety of amines have also been described. The IR spectra of various nitro complexes of Ru(II) [90], Pd(II) [91,92], Pt(II) [78,85,92–95] and Pt(IV) [96] have also received attention, and the Raman spectra of several Pd(II) and Pt(II) compounds [86,91] have been described.

The overall trends in the IR spectra accompanying nitro coordination are apparent from the data listed in Table 2, and may be seen in the spectra of the ions $M(NO_2)_6^{n-}$ [M = Cd(II), Ni(II), Co(II) and Co(III)] shown in Fig. 11. The trends in the energies of ν_s and ν_{as} are shown schematically in Fig. 12. The most pronounced effect is a significant increase in the energy of the antisymmetric stretch, which occurs at higher energy than the symmetric stretch in the nitro complexes formed by Pd(II), Pt(II) and all trivalent and tetravalent metal ions. The shift from the free-ion value increases along the series Cd(II) < Ni(II) < Co(III) < Pt(II) < Pt(IV), presumably as a result of a progressive strengthening of the metal–nitrite bond. The intensity of the peak due to ν_s also increases along this series. The spectra of the $Cu(NO_2)_6^{4-}$ and $Co(NO_2)_6^{4-}$ ions are unusual, in that they show two intense peaks (at ~ 1280 and ~ 1330 cm^{-1} with two weak shoulders at ~ 1300 and ~ 1340 cm^{-1}) in the region due to ν_s and ν_{as} (Fig. 11). The two stronger peaks have been interpreted as being due to ν_s and ν_{as}, the weaker shoulders being due to a lattice splitting effect [97]. However, it seems more likely that the more

TABLE 2

Vibrational frequencies for typical complexes containing nitrite groups coordinated in different ways

Compound	Coordination type[a]	Vibrational energies (cm^{-1})			Ref.
		ν_{as}	ν_s	δ_{NO_2}	
$NaNO_2$	Ionic	1250	1335	830	18
$K_2CaNi(NO_2)_6$	Nitro	1355	1325	834	71
$K_3Co(NO_2)_6$	Nitro	1390	1328	833	78
$K_2Pt(NO_2)_4$	Nitro	1440, 1415	1392, 1344	845, 838	78
$K_2Pt(NO_2)_4Br_2$	Nitro	1475, 1460	1328	842	78
$Ni(NNN'N'\text{-tetmen})(NO_2)_2$	Chelating	1200	1289	863	42
$Cs_2Zn(NO_2)_4$	Type (iii) *O* nitrito	1381	1167	847	33
$Ni(NN\text{-dimen})_2(NO_2)_2$	Type (ii) *O* nitrito	1387	1130	817	22
$[Co(NH_3)_5(NO_2)]^{2+}$	Type (ii) *O* nitrito	1468	1065	825	18
$[Pt(NH_3)_5(NO_2)]^{3+}$	Type (ii) *O* nitrito	1505	995	850	163
$[Ni(3\text{-mepy})_2(NO_2)_2]_3 \cdot C_6H_6$	Type (vii) $\mu(O)$ bridging	1460	1019	[b]	44
$[N(CH_3)_4]Ni(NO_2)_3$	Type (v) $\mu(NO)$ bridging	1435	1202	852	7
$[Co(NH_3)_3(OH)_2(NO_2)]_2^{3+}$	Type (v) $\mu(NO)$ bridging	1516	1200	830	18

[a] For details of coordination type see Fig. 1. [b] Peak unassigned.

complicated spectra are attributable to the fact that these complexes each involve a metal ion which is susceptible to Jahn–Teller distortion (see section G), having four short and two long bonds (~2.0 and 2.2 Å, respectively). The peaks at ~1330 and ~1340 cm^{-1} (which occur at energies very similar to those in the analogous $Ni(NO_2)_6^{4-}$ ion) are then due to ν_{as} and ν_s of the four more strongly bound nitro groups, while the less intense peaks at ~1280 and ~1300 cm^{-1} are due to ν_{as} and ν_s of the two more weakly bound groups. It is interesting to note that this doubling of the IR frequencies occurs even when the complexes crystallize with a structure where X-ray diffraction indicates six equal M–N bond distances [98]; the implications of this on the nature of the species present in these lattices are discussed in section E(iii). The wagging mode δ_{NO_2} is apparently not greatly affected by nitro coordination as such, though this peak often exhibits splittings which have been interpreted in terms of the site symmetry in the polynitrite complexes [71,73,97], or the symmetry of the complex in mixed-ligand nitrite complexes [70,80–82].

The metal–ligand vibrational frequencies of nitro complexes have also received considerable attention, and a complete assignment of these is available for $Co(NO_2)_6^{3-}$ and $Ni(NO_2)_6^{4-}$ (Table 3) [71]. Nitro groups characteristically exhibit an out-of-plane wagging mode which occurs at rather high energy (~625 cm^{-1} for complexes of Co(III), Pt(II) and Pd(II), and ~425 cm^{-1} for complexes of divalent metal ions). No analogous peak is

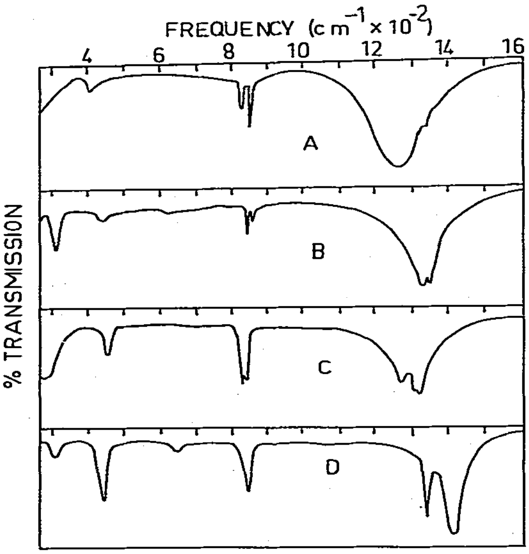


Fig. 11. IR spectra of some hexanitro complexes [182]: A, $Cs_2SrCd(NO_2)_6$; B, $K_2BaNi(NO_2)_6$; C, $K_2SrCu(NO_2)_6$; D, $Rb_3Co(NO_2)_6$.

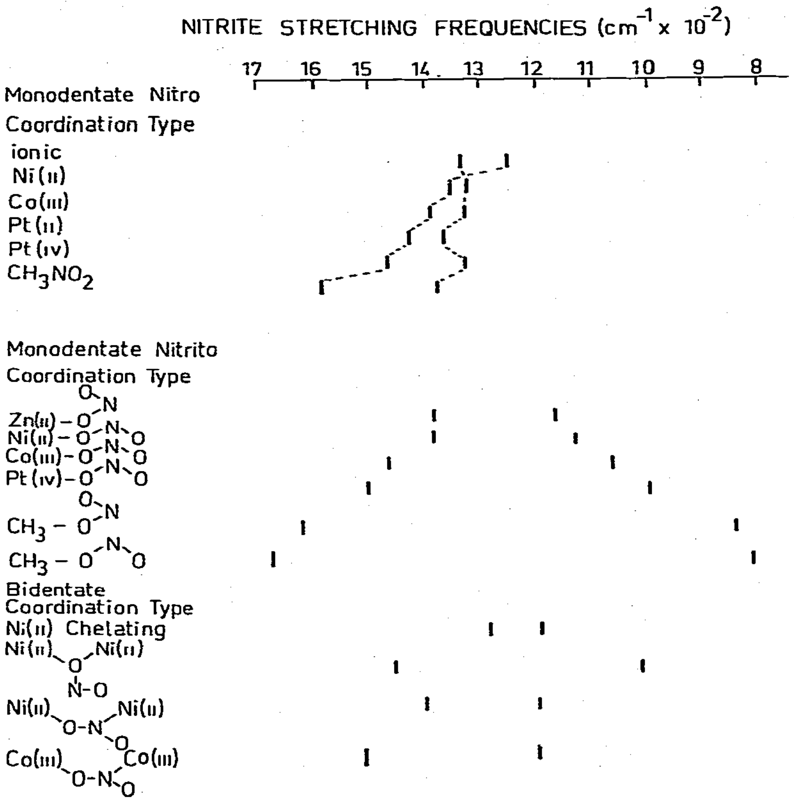


Fig. 12. Diagram showing how the vibrational stretching frequencies of the nitrite ion depend upon the way it is coordinated.

TABLE 3

Assignment of the vibrational spectra of the $Co(NO_2)_6^{3-}$ and $Ni(NO_2)_6^{4-}$ ions. Data from ref. 71

Vibrational mode	Type	Vibrational energy (cm^{-1})	
		$K_3Co(NO_2)_6$	$K_2CaNi(NO_2)_6$
ν_1	NO_2 asymmetric stretch	1386	1355
ν_2	NO_2 symmetric stretch	1332	1325
ν_3	NO_2 scissor	827	834
ν_4	NO_2 wag	637	458
ν_5	M–N stretch	416	284
ν_6	NO_2 rock and skeletal deformation	293	255
ν_7	Skeletal deformation and lattice mode	195	192
ν_8	Skeletal deformation and lattice mode	154	176
ν_9	Lattice mode	132	135
ν_{10}	Lattice mode	106	105

observed in this region for nitrito complexes, so that it has been suggested [69,72] that the presence of this absorption is a useful indication of nitro rather than nitrito coordination of the nitrite group. The antisymmetric M–N stretching frequencies have been assigned in the region of 400 cm^{-1} for nitro complexes of Pt(II), Pd(II) [78] and trivalent metal ions such as Co(III) [71], and at ~300 cm^{-1} in nitro complexes of the divalent metal ions of the first transition series [71,78], these energies being some 10% lower than those observed for the M–N stretches in the analogous hexamine complexes [99]. The assignment of ν_{as} (M–N) at ~425 cm^{-1} and ρ_w at ~600 cm^{-1} for the ion $M(\mathit{N}O_2)_6^{4-}$ (M = Fe, Co, Ni, Cu) by Elliott et al. [77] would seem to be in error [107], the peaks at ~600 cm^{-1} possibly being due to the first overtones of the M–N stretches at ~300 cm^{-1} and the peaks at ~425 cm^{-1} being due to ρ_w (NO_2).

(b) Monodentate nitrito coordination

Although not studied as extensively as complexes containing the nitro group, the IR frequencies of type (ii) nitrito groups (in which the non-bonded oxygen is *trans* to the metal) bound to a variety of metal ions have been reported. In particular, several studies have been made of the spectra of various amine complexes of cobalt(III) [69,81,100–102] and chromium(III) [17–19] containing nitrite ions bound in this way, as well as of a series of pentamine complexes of Pt, Ir, Os, Rh and Cr in which isotopic substitution was used to unambiguously identify the peaks due to the nitrite ligand [87]. The IR spectra of various nickel(II) nitrito complexes of general formula $Ni(diamine)_2(\mathit{O}NO)_2$ and $NiL_4(\mathit{O}NO)_2$ have also been reported, where diamine is a substituted ethylenediamine and L an aromatic amine [22,25]. While the presence of type (ii) nitrito linkages has been confirmed in the complexes formed by *NN*-dimethyl-ethylenediamine [14], pyridine [28] and 4-methylpyridine [28], it has been found that the compounds $Ni(\mathit{NN'}\text{-dieen})_2(NO_2)_2$ [31] and $Ni(\mathit{m}\text{-stien})_2(NO_2)_2$ [30] in fact each contain one chelating and one ionic nitrite group. The IR spectra of a series of complexes of general formula $NiL_2(NO_2)_2$ (L = one of a range of ligands such as 2-aminopyridine) have also been interpreted [32] in terms of monodentate nitrito coordination of the anions. However, as the peak energies are similar to those observed for chelating nitrite groups (see following section) this conclusion must be treated with caution. The IR spectra of various zinc(II) [24] and cobalt(II) [23] nitrite complexes have been interpreted as indicating nitrito coordination, as has the spectrum of $(CN_3H_6)_3[UO_2(C_2O_4)_2(NO_2)]$ [103]. In the case of $Zn(\mathit{NN}\text{-dimen})_2(\mathit{O}NO)_2$ X-ray studies have confirmed that type (ii) nitrito coordination is present [27].

The vibrational energies typical of type (ii) nitrito coordination to various metal ions are listed in Table 2, and shown schematically in Fig. 12. It may be seen that this manner of bonding has a quite different effect on the stretching frequencies from nitro coordination, these modes diverging from the free-ion values towards the NO single- and double-bond frequencies observed in CH_3ONO. The magnitude of the difference between them increases along the series: $Zn(II) < Ni(II) < Co(III) \sim Cr(III) \sim Pt(II) < Pt(IV)$, this sequence paralleling the expected increase in the metal–ligand bond strength. Monodentate nitrito coordination also causes a large increase in the intensity of the highest energy peak in the nitrite IR spectrum, compared with the free ion. As with nitro coordination, the energy of the δ_{NO_2} wagging mode undergoes no significant systematic shift when the nitrite bonds via a single oxygen atom.

Type (iii) nitrito coordination (see Fig. 1) has been definitely established in only a few complexes of copper(II) and zinc(II) (see section C) so that generalizations concerning the IR frequencies associated with this type of coordination must be considered tentative. The IR spectrum of the $Zn(ONO)_4^{2-}$ ion, shown in Fig. 10, has peaks due to the nitrite stretching modes at 1185 and 1380 cm^{-1}, somewhat closer to the free-ion values than those observed [24] for the type (ii) nitrito groups in Zn(*NN*-dimen)$_2$(*O*NO)$_2$. Copper(II) complexes containing type (iii) nitrito groups also typically show peaks at ~1180 and ~1350 cm^{-1} [36,104], so that peaks in the range 1170–1190 cm^{-1} and 1350–1380 cm^{-1} may well be characteristic of this type of nitrite coordination. The relatively small divergence of the stretching frequencies is consistent with the second oxygen atom of the nitrite being "semi-coordinated" to the metal, and as mentioned, this type of monodentate nitrito coordination may also be considered as a highly asymmetric form of chelation.

It should be noted that hydrogen bonding can also affect the nitrite vibrational frequencies. Thus, hydrogen bonding to the *trans* oxygen atom of a type (ii) nitrito group might well have the effect of shifting the stretching frequencies into the range normally associated with a type (iii) nitrito group, or even a chelating nitrite ion. Reliance upon vibrational spectroscopy alone to deduce the manner of nitrite coordination could therefore sometimes prove misleading. For instance, the compound Ni(pyr)$_4$(*O*NO)$_2$ exhibits nitrite stretching peaks at 1140, 1330 and 1390 cm^{-1} [28], from which it might be concluded that it contains both nitro and monodentate nitrito groups, as has been proposed [25] for the analogous complex Ni(i-quin)$_4$(NO_2)$_2$ (see section G). However, the electronic spectrum of Ni(pyr)$_4$(*O*NO)$_2$ is consistent with its formulation as a simple nitrito complex, and this has been confirmed by an X-ray structure analysis [28]. The nitrite atoms not bound to the metal, however, form quite short hydrogen bonds to the pyrazole NH groups, and it has been suggested [28] that this may shift the stretching frequencies away from the positions normally characteristic of monodentate nitrito coordination. Similar arguments may also apply to the complex Ni[2-(aminomethyl)py$_2$]$(NO_2)_2$ which also shows peaks in the ranges normally associated with both nitrito and nitro groups, but has an electronic spectrum characteristic of the presence of nitrite groups bound solely via oxygen [32].

(c) Chelation

The IR spectra of various complexes of the type $ML_2(O_2N)_2$, M = Ni [42], Co [42,108], and Zn [24], thought to contain chelating nitrito groups have been reported, where L represents either an aromatic monodentate amine, $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$, or L_2 a substituted ethylenediamine. Chelation of the nitrite groups has been confirmed in the complexes M(*NNN'N'*-tetmen)$(O_2N)_2$, M = Ni [38,41] and Zn [38]. The observed peak energies are quite similar to those obtained for the chelated nitrites in the tetranitrite complexes of Mn(II), Cd(II) and Hg(II) [33]. The IR spectra of $K_2Cd(O_2N)_4$ and $Cs_2Mn(O_2N)_4$ are shown in Fig. 10, while typical frequencies for chelated nitrito groups are shown in Table 2. From these it may be seen that chelation has comparatively little effect on the nitrite stretching frequencies, these often being reduced marginally in energy with respect to the free ion. Also, the peak due to ν_s remains very weak in the IR spectrum, and sometimes cannot be resolved from the intense absorption due to ν_{as} [see spectrum due to $K_2Cd(O_2N)_4$]. The wagging mode δ_{NO_2}, on the other hand, tends to increase in energy by 25–40 cm^{-1} on chelation.

The two metal–oxygen distances of a chelated nitrite group often differ significantly, and this is in fact the case for two of the groups in $K_2Cd(O_2N)_4$ [Fig. 4(a)]. In this compound the only detectable effect on the vibrational spectrum is a splitting of the sharp peak due to δ_{NO_2}. However, in general, unsymmetrical chelation is expected to produce a widening of the energy separation between ν_s and ν_{as} towards the values observed for monodentate nitrito coordination. A quantitative comparison between the difference in the metal–oxygen bond lengths and the NO stretching frequencies carried out by Finney et al. for a number of copper(II), nickel(II) and zinc(II) complexes supports this suggestion [38].

(d) (NO) *Bridging*

The IR frequencies of nitrite groups bridging via nitrogen and oxygen, with the metal ion *cis* with respect to the bridging group [Fig. 1(v)], have been reported for various amine complexes of cobalt(III) [18,70] and nickel(II) [51,52], and also for the compound $[N(CH_3)_4]Ni(NO_2)_3$ which probably contains metal ions linked by groupings of this kind [7]. The characteristic peak energies for this type of nitrite coordination are listed in Table 2 and shown schematically in Fig. 12. As might be expected, the shifts in the NO stretching frequencies from their free-ion values are a combination of the effects observed for monodentate nitro and nitrito coordination, with the separation between these increasing markedly and their mean being raised significantly in energy. The effects are more pronounced when the nitrite is bound to cobalt(III) than to nickel(II). The wagging mode δ_{NO_2} is also often raised slightly in energy. So far, the vibrational frequencies of nitrite groups bridged via nitrogen and oxygen with the metals *trans* with respect to the nitrite [Fig. 1(vi)] have been reported only for the isomorphous compounds $[Ni(en)_2(NO_2)]$ X, X = BF_4 [52], ClO_4 [53]. The peak energies are similar to those observed for the type (v) nitrite groups bridging between nickel(II) ions, except that both stretching frequencies are closer to their free-ion values. This may well reflect the comparatively long Ni–N and Ni–O bond lengths present in the complex [38], so that until data are available from more complexes containing this type of nitrite linkage it is hard to say whether vibrational spectroscopy will provide a means of distinguishing between the two types of (*NO*) nitrite bridge.

(e) μ(O) Nitrito bridges

The IR frequencies of nitrite ions bridging via a single oxygen atom have so far been reported only for these groups in a series of oligomers of general stoichiometry $NiL_2(NO_2)_2 \cdot xC_6H_6$ [52], where L is a monodentate aromatic amine, and in the pentamer Ni_5(*NN*-dimen)$_4(NO_2)_8(OH)_2$ [51]. The energies of the stretching frequencies (~ 1020 and ~ 1430 cm^{-1}) indicate shifts from the free-ion values similar in kind, but greater in magnitude, to those observed for monodentate nitrito coordination to nickel(II). The stretching frequencies for a nitrite bridging two nickel(II) ions via a single oxygen are in fact quite similar to the values observed for a monodentate nitrito group bound to a trivalent metal ion (Table 2, Fig. 12).

(f) Relationship between the vibrational frequencies and the internal geometry of the nitrite ion

Now that crystal structure determinations have been carried out on a fairly large range of nitrite complexes it is of interest to see how well the structural parameters correlate with the vibrational frequencies of the nitrite ion considering the whole range of coordination types. The wagging mode δ_{NO_2} might be expected to be related to the ONO angle but experimentally no systematic trends are observed for this mode, except a tendency towards an increase in energy when the nitrite group chelates.

The most profound changes to occur when the nitrite coordinates to one or more metal ions take place when the equivalence of the two oxygen atoms is destroyed. As expected, it is then observed that the N–O bond distance involving the oxygen atom closer to the metal increases in length, while that

TABLE 4

Vibrational stretching frequencies and NO bond lengths for nitrite groups coordinated in various ways

Compound	NO Bond lengths (Å)	NO stretching frequencies (cm^{-1})	Diff. (cm^{-1})	Ref.
$NaNO_2$	1.240(3)	1261, 1328	67	57, 63
Ni(*NNN'N'*-tetmen)$(NO_2)_2$	1.258(4), 1.238(4)	1200, 1289	89	38, 42
	1.260(4), 1.235(4)			
Zn(*NNN'N'*-tetmen)$(NO_2)_2$	1.258(4), 1.260(3)	1183, 1316	133	38, 24
	1.267(4), 1.250(4)			
Cu(bipy)$(NO_2)_2$	1.27(1), 1.22(2)	1150, 1372	222	37
Zn(*NN*-dimen)$_2(NO_2)_2$	1.302(5), 1.141(6)	1145, 1380	235	27, 24
Ni(*NN*-dimen)$_2(NO_2)_2$	1.288(3), 1.215(3)	1130, 1387	257	14, 22
Ni_3(3-mepy)$_6(NO_2)_6 \cdot C_6H_6$	1.305(4), 1.197(4)	1019, 1460	441	43, 52
	1.259(3), 1.230(4)	1236, 1412	176	
$Ni_5en_8(NO_2)_8(OH)_2$	1.274(8), 1.224(8)	1240, 1430	190	51
$[Co_2(NH_3)_6(OH)(NO_2)_2]Cl_3 \cdot H_2O$	1.290, 1.212	1200, 1516	316	189, 18
	1.300, 1.203			
cis-CH_3ONO	1.398(5), 1.182(5)	844, 1625	781	60, 190
trans-CH_3ONO	1.415(5), 1.164(5)	814, 1681	867	60, 190

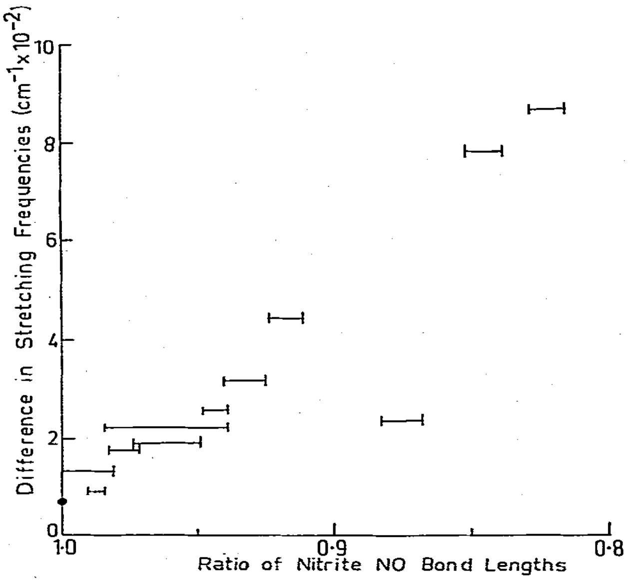


Fig. 13. The difference in energy of the nitrite vibrational stretching frequencies plotted against the ratio of the nitrite N–O bond lengths. The data are from Table 4.

to the less strongly bound oxygen decreases, the limiting values being those observed in the *cis* and *trans* forms of methyl nitrite (see Table 4). A concomitant change in the NO stretching frequencies is expected, with these diverging towards the NO single- and double-bond frequencies observed for CH_3ONO. The separation in the stretching frequencies is shown plotted against the ratio of the two N–O bond lengths in Fig. 13 for all compounds containing chelated, asymmetrically chelated, monodentate nitrito and bridging nitrite groups where both the nitrite geometry is accurately known and the vibrational frequencies are unambiguously established. It is apparent that an approximately linear relationship does exist between these parameters, with the maximum perturbation in a nitrite complex (coordination to two nickel(II) ions via a single oxygen atom) being about half that due to the alkyl group in methyl nitrite. It would thus seem that in overall terms the vibrational frequencies and structural parameters of the nitrite ion correlate fairly well, which may explain why IR spectroscopy has generally proved so successful as a means of deducing the manner of nitrite coordination in metal complexes.

(ii) Electronic spectroscopy

The electronic spectrum of the uncoordinated nitrite ion has been extensively studied, both in crystals of $NaNO_2$ [64,109,110], and in various solvents [111–113]. The spectrum consists of an intense absorption centred at 47000 cm^{-1} assigned as the $\pi \rightarrow \pi^*$ transition, and a much weaker band ($\epsilon_{molar} \sim 301$ mol^{-1} cm^{-1}), centred at ~28000 cm^{-1} assigned as an $n \rightarrow \pi^*$ transition. The latter band shows extensive vibrational fine structure at low temperature, largely in the wagging mode δ_{NO_2} which has an energy of ~600 cm^{-1} in the excited electronic state [64]. The nature of the non-bonded orbital involved in this transition has been the subject of some argument, but the general concensus is that this is probably localized largely on the nitrite oxygen atoms [111,114,115]. As will be discussed, the electronic spectra observed for certain nickel(II) nitro complexes lend support to this conclusion [30,116].

The position of the nitrite ligand in the spectrochemical series is quite different when it bonds to a metal via oxygen from that when it coordinates via nitrogen. Oxygen coordination produces a comparatively weak perturbation, while when it bonds via nitrogen the nitrite acts as a strong ligand [117]. The measurement of the electronic spectrum can therefore act as a useful guide to the nature of the metal–nitrite linkage in a complex. However, recent studies suggest [116,118–120] that charge-transfer and internal nitrite transitions also occur at comparatively low energy in many nitrite complexes, making the detailed interpretation of the spectra more complicated than earlier studies had suggested. The results obtained for complexes of various different metal ions are considered below.

(a) Chromium(III)

The electronic spectra of several complexes of chromium(III) nitrite with amine ligands have been reported by Fee et al. [17,121], the nitrite in these invariably being coordinated as a monodentate group via oxygen. The first spin-allowed "*d–d*" transition in these compounds occurs at ~21000 cm^{-1} and is shifted to lower energy compared with the corresponding band in the $Cr(NH_3)_6^{3+}$ ion, suggesting that the nitrito group lies lower in the spectrochemical series than ammonia when bound to chromium(III). A number of these complexes also show a weak band at ~28000 cm^{-1} ($\epsilon \approx 251$ mol^{-1} cm^{-1}) which shows vibrational fine structure. The progressional energy of this (~600 cm^{-1}) is characteristic of the δ_{NO_2} nitrite wagging mode in an excited state in which an electron has been transferred to the nitrite π^* orbital, and the band was consequently assigned as an $n \rightarrow \pi^*$ internal nitrite transition. Since the nitrite is coordinated via oxygen in the complexes, it was suggested that the non-bonded orbital involved in the transition is probably located on the nitrogen atom; however, recent work on other systems suggests that this may in fact not be the case (see section on nickel complexes).

(b) Cobalt(III)

The electronic spectra of the linkage isomers of formula $[Co(NH_3)_5(NO_2)]^{2+}$ have been studied by several workers [17,81,121,122]. The first spin-allowed transition of the unstable nitrito form of this ion occurs at 20580 cm^{-1}, while that of the nitro isomer is at 21860 cm^{-1}. When compared with the value of 21100 cm^{-1} observed for the $Co(NH_3)_6^{3+}$ ion [117] this suggests Δ values of ~26000 and ~18000 cm^{-1} for the monodentate nitro and nitrito groups bound to cobalt(III). The spectra of the various *cis* and *trans* isomeric forms of the $[Co(en)_2(NO_2)_2]^+$ ion have also been reported [122], as have the spectra of mixed-ligand nitro complexes of cobalt(III) involving several planar macrocyclic ligands [125], the acetylacetonate anion [126–129], bipyridyl [129] and ammonia [79]. For a number of complexes of the type $Co(acac)_2(NO_2)$(amine), in addition to the "*d–d*" transition at ~18500 cm^{-1}, bands were observed at ~30000 and ~37000 cm^{-1} and these were assigned as metal → ligand and internal ligand $\pi \rightarrow \pi^*$ transitions, respectively [128]. However, in view of the fact that it is well established [110–113] that nitrite $n \rightarrow \pi^*$ internal nitrite transitions are expected in the region 25000–30000 cm^{-1}, and that it has been proposed that nitrite → metal charge-transfer transitions also occur at low energy in cobalt(III) nitro complexes [119], the assignment of the peak at 30000 cm^{-1} must be considered tentative. The electronic spectrum of the hexanitro ion $Co(NO_2)_6^{3-}$ exhibits a peak at 21500 cm^{-1} and this was assigned initially to the first spin-allowed "*d–d*" transition. However, it has been pointed out by Caulton and Fenske [119] that this implies a Δ value for the nitro group much lower than that suggested by the electronic spectrum of ions such as $[Co(NH_3)_5(NO_2)]^{2+}$. From an investigation of the spectra of a range of complexes of the form $[Co(NH_3)_n(NO_2)_{6-n}]$ these authors conclude that as the number of nitro groups bound to the metal increases, not only does the $^1T_{2g} \leftarrow {}^1A_g$ "*d–d*" transition move to higher energy in a regular manner, but that a second band of comparable intensity moves into the visible region of the spectrum, and it is this second peak which is observed at 21500 cm^{-1} in the spectrum of $Co(NO_2)_6^{3-}$, with the lowest energy "*d–d*" transition being masked under the intense absorption due to a metal → ligand charge-transfer transition centred at ~27000 cm^{-1}. On the basis of molecular-orbital calculations and a comparison of the spectra with those of the hexanitro complexes of other metal ions these authors proposed that the "visible" band in $Co(NO_2)_6^{3-}$ is in fact probably due to a ligand → metal charge-transfer transition.

(c) Cobalt(II)

The electronic spectrum of the $Co(NO_2)_6^{4-}$ ion has been reported in various crystal lattices [77,123,124]. The low-spin d^7 electron configuration of the metal in this complex is expected to produce a strong Jahn–Teller distortion. While this is indeed observed in some compounds containing the ion, others exhibit an apparently regular octahedral geometry [130]. The electronic spectra of all these compounds are very similar [123], and are consistent with a tetragonally distorted arrangement of nitro groups similar to that observed in $K_2BaCo(\mathit{N}O_2)_6$ at 140 K, with four Co–N bond lengths of 1.92 Å and two of 2.10 Å [236]; possibly the apparently regular octahedral complexes contain a disordered arrangement of tetragonally distorted complexes, perhaps in a state of dynamic equilibrium. The spectra of the compounds consist of three peaks, centred at ~8000, 15000 and 22000 cm^{-1}. The first two bands have been assigned by Reinen and Friebel as each being due to the superposition of various "*d–d*" transitions of the cobalt(II) in a tetragonal ligand environment [124]. The peak energies suggest *d*-orbital energies which imply a value of $\Delta_0 = 12600$ cm^{-1} for the nitro group towards cobalt(II) in a regular octahedral complex. This agrees well with the value of $\Delta \approx 13000$ cm^{-1} observed for the $Ni(\mathit{N}O_2)_6^{4-}$ ion [124], being about half that value obtained for the nitro group towards cobalt(III). This ratio is consistent with that observed for other ligands [e.g. $\Delta(H_2O) = 8900$ cm^{-1} for cobalt(II) and 18800 cm^{-1} for cobalt(III)].

The electronic spectra of several cobalt(II) complexes with various amine ligands thought to have essentially octahedral geometries and to contain monodentate nitrito groups have been reported by Goodgame et al. [23]. The peak energies of these suggest a ligand-field strength of the nitrito group towards cobalt(II) corresponding to a Δ value of ~ 8000 cm^{-1}. Again, this is about half the value observed for this ligand towards cobalt(III). The spectra of a number of complexes of the type $Co(L)_2(NO_2)_2$ have been described [23], where L is a monodentate ligand such as an aromatic amine or $(C_6H_5)_3PO$. The IR spectra suggest that the nitrite groups in these compounds chelate, though it is not certain whether the chelation is symmetrical or unsymmetrical. The band energies and intensities imply a highly distorted ligand coordination geometry in the complexes. It was suggested [23] that the effective ligand perturbation on the cobalt(II) ion is intermediate between the octahedral situation expected for three bidentate ligands and the tetrahedral environment which would result if each chelating nitrite ion is considered to occupy a single coordination site about the metal. The spectrum of the $Co(\mathit{O}_2N)_4^{2-}$ ion, which is thought to contain chelating nitrito groups, also shows peaks which are intermediate in energy and intensity between those normally associated with an octahedral and a tetrahedral ligand environment [33].

(d) Nickel(II)

The electronic spectra of a large number of nitrite complexes of this metal have been reported, involving a variety of different coordination modes. The spectrum of the hexanitro ion $Ni(NO_2)_6^{4-}$ has been measured by several groups of workers [7,22,77,131]. In the visible region, this consists of two peaks centred at ~13000 and ~21000 cm^{-1} and most authors have assigned these to the first two spin-allowed transitions of octahedrally coordinated nickel. However, it has been noted by Reinen et al. [131] that the band energies vary according to the nature of the counter-cation, the first transition decreasing from 13300 cm^{-1} in $K_2CaNi(NO_2)_6$ to 12000 cm^{-1} in $Cs_2BaNi(NO_2)_6$. Instead of showing a corresponding decrease in energy, the band at 21500 cm^{-1} in the former compound splits into two bands, centred at 19500 and 21500 cm^{-1}, in $Cs_2BaNi(NO_2)_6$. The authors concluded that the peak at 19500 cm^{-1} in the latter compound is due to the "*d–d*" transition $^3T_{1g}(F) \leftarrow {}^3A_{2g}$, while the band centred at 21500 cm^{-1} is a charge-transfer transition. Caulton and Fenske [119], in a paper on the electronic spectra of a range of hexanitrometallates, also concluded that the band centred at ~20500 cm^{-1} in $Ni(NO_2)_6^{4-}$ is predominantly due to an electron-transfer transition.

Further evidence on this question is provided by recent studies of the electronic spectra of a number of mixed-ligand nickel(II) complexes containing nitrite groups bound via nitrogen. The spectra of a variety of nitro complexes of the type $Ni(diamine)_2(NO_2)_2$ have been reported [88], as have

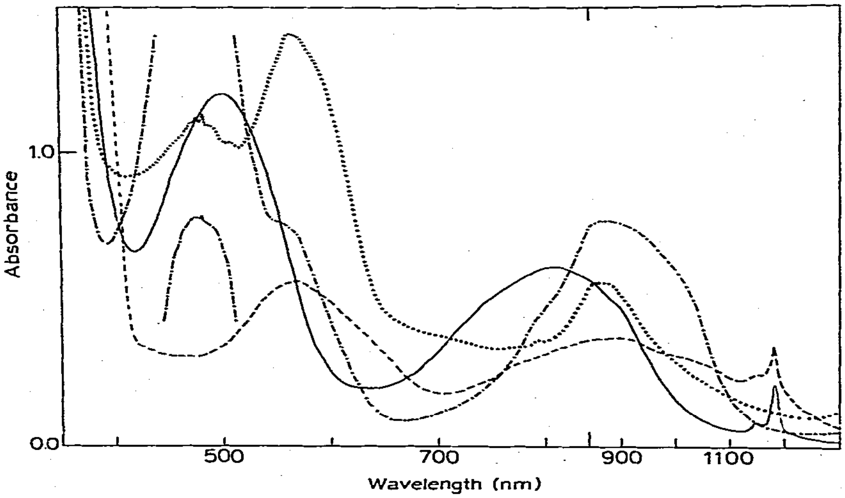


Fig. 14. Electronic spectra of mulls of Ni(*NN*-dimen)$_2$(*O*NO)$_2$ (dashed line) and [Ni(*NN'*-dimen)$_2$(*N*O$_2$)$_2$]·H$_2$O (full line), and a single crystal of [Ni(*NN*-dimen)(*N*O$_2$)(H$_2$O)]ClO$_4$ with the electric vector of polarized light along the two extinction directions of an arbitrary crystal face (dotted and dash-dotted lines). All spectra measured at 7 K. Note the change in wavelength scale at 840 nm [116].

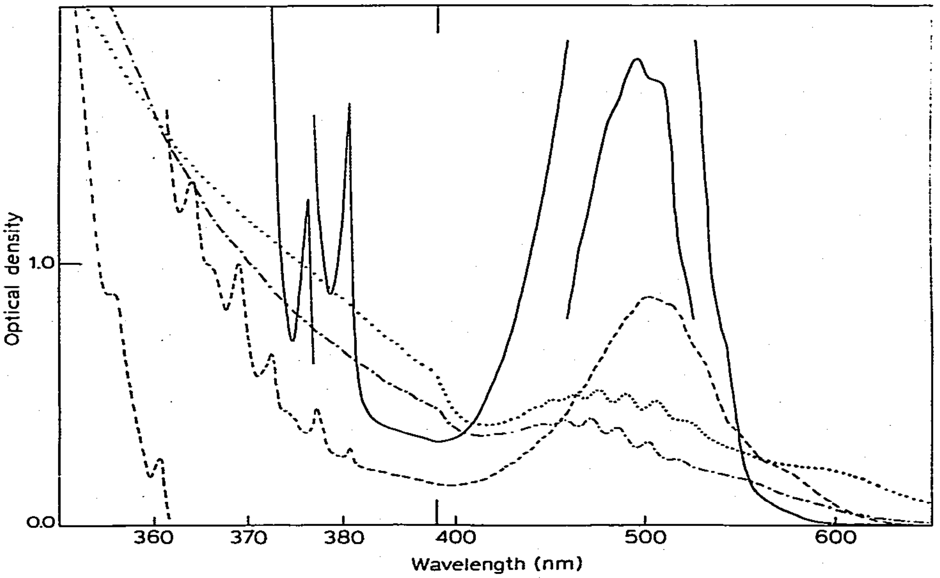


Fig. 15. Electronic spectra of single crystals of $[Ni(m\text{-stien})_2(NO_2)(H_2O)]ClO_4$ (dotted and dash-dotted lines) and $Ni(NH_3)_4(NO_2)_2$ (dashed and full line) with the electric vector of polarized light along the two extinction directions of each crystal face. Spectra measured at 7 K [30,134].

the spectra of a number of complexes containing (*NO*)-bridged nitrite groups [52]. Single-crystal polarized spectra of the *trans* nitro complexes $Ni(NH_3)_4(NO_2)_2$ [132] and $Ni(en)_2(NO_2)_2$ [133] have also been described. In all these studies the bands centred at ~ 12500 and ~ 20000 cm^{-1} were interpreted as being due to the transition $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ of essentially octahedrally coordinated nickel(II), the peaks being sometimes split by a tetragonal component to the ligand field. The spectrum of a typical complex of this kind, $[Ni(NN'\text{-dimen})_2(NO_2)_2] \cdot H_2O$, is shown in Fig. 14. However, recent measurements [30,116,134] of the spectra of single crystals of several nitro complexes at low temperature have revealed vibrational fine structure on the band at ~ 20000 cm^{-1}. The spectra of two such complexes, *trans*-$Ni(NH_3)_4(NO_2)_2$ and *trans*-$[Ni(m\text{-stien})_2(NO_2)H_2O)]ClO_4$ are shown in Fig. 15. The progressional energy of ~ 600 cm^{-1} is too high for the active vibration to be assigned to a metal–ligand mode, but is comparable to the spacings observed [64] on the band centred at ~ 28000 cm^{-1} in the spectrum of $NaNO_2$. In the latter compound the peaks have been assigned to the δ_{NO_2} nitrite wagging mode in an excited electronic state in which an electron has been promoted to the nitrite π^* orbital. It therefore seems highly likely that the bulk of the intensity in the peak at ~ 20000 cm^{-1} in nickel(II) complexes containing nitrogen-bonded nitrite groups derives not from a "*d–d*" transition but from a transition in which an electron is excited to the nitrite π^* orbital. This conclusion is strengthened by the electronic spectrum observed [116] for the nitro complex *cis*-[Ni(*NN*-dimen)$_2$-(*N*O$_2$)(H$_2$O)]ClO$_4$ shown in Fig. 14. In this compound the higher-energy band is split into two components, centred at 17800 and 21000 cm^{-1}, with the latter band showing a poorly resolved progression of ~600 cm^{-1}. The $^3T_{2g} \leftarrow ^4A_{2g}$ transition occurs at ~11000 cm^{-1} in this complex, which is consistent with the band at 17800 cm^{-1} being due to the second spin-allowed transition $^3T_{1g}(F) \leftarrow ^3A_{2g}$ and that at 21000 cm^{-1} being non-*d*–*d* in origin. This latter band could be caused by a spin-forbidden internal nitrite transition [135], but it seems more likely [116] that it is due to a weakly allowed metal → ligand charge-transfer transition which happens to have an intensity comparable to a "*d*–*d*" transition. The low intensity of the band may be due to the fact that the highest-energy partly filled metal e_g^* orbital has zero overlap with the nitrite π^* orbital in the absence of vibronic coupling. It may also be noted that when the nitrite bonds to a metal via oxygen, the π^* orbital lobes are not directed along the bond axis, which is consistent with the fact that the band at ~20000 cm^{-1} is not observed in complexes solely containing nitrite groups bound to nickel(II) via oxygen. The complex Ni(NH$_3$)$_4$(*N*O$_2$)$_2$ also shows a band with an origin at ~25000 cm^{-1} very similar in energy and the nature of the vibrational fine structure to that observed in NaNO$_2$. This is presumably due to an internal nitrite $n \rightarrow \pi^*$ transition, and confirms that the electron probably originates from orbitals localized on the nitrite oxygen atoms, since the nitrogen lone-pair electrons are involved in bonding to the metal in the amine complex.

The electronic spectra of various complexes of the type Ni(diamine)$_2$-(*O*NO)$_2$ and Ni(L)$_4$(*O*NO)$_2$ containing monodentate nitrito groups have been reported by Goodgame and Hitchman [22,25], and Finney et al. [28,29], where diamine represents a substituted ethylenediamine and L an aromatic amine. It should be noted that in this series the complexes Ni(*m*-stien)$_2$(NO$_2$)$_2$ and Ni(*NN'*-dieen)$_2$(NO$_2$)$_2$ previously formulated as simple nitro complexes [22] are now known to each contain one chelating and one ionic nitrite group [30,31]. Single-crystal polarized spectra have been reported for the complexes Ni(*NN*-dimen)$_2$(*O*NO)$_2$ and Ni(*NN*-dieen)$_2$(*O*NO)$_2$ [118]. All these compounds show the three spin-allowed transitions in the regions ~10000, ~17000 and ~25000 cm^{-1} expected for nickel(II) in an essentially octahedral ligand environment. The bands are often split into two components, and an analysis of the separation of these allows the ligand-field splitting parameter of the nitrito group to be estimated. This has been found to be $\Delta_0 \simeq 8900$, 8300 and 6900 cm^{-1} in the complexes [Ni(py)$_4$(*O*NO)$_2$]·2py [28], Ni(pyr)$_4$(*O*NO)$_2$ [28] and Ni(2-meim)$_4$(*O*NO)$_2$ [29], respectively, the progressive decrease paralleling the increasing average Ni–O bond lengths observed in the three complexes (2.04, 2.11 and 2.15 Å, respectively). The nitrito group bound to nickel(II) thus produces a ligand-field splitting only 50–70% as large as that of a nitro group ($\Delta_0 \simeq 13000$ cm^{-1}), the ratio of the splitting parameters being in fact similar to that observed for these ligands bonded to cobalt(III).

Spectra have also been reported for various compounds of the type Ni(diamine)(O_2N)$_2$ and Ni(L)$_2$(O_2N)$_2$ containing chelating nitrite groups [42,118], where diamine is a heavily substituted ethylenediamine and L an α-substituted pyridine. In contrast to the analogous cobalt(II) complexes, the spectra show little evidence of a marked departure from a regular octahedral ligand coordination geometry. Single-crystal polarized spectra have been measured [118] for the complexes [Ni(*NN'*-dieen)$_2$(O_2N)]NO$_2$, [Ni(*NNN'N*-tetmen)(O_2N)]NO$_2$, [Ni(*NN'*-dieen)$_2$(O_2N)]BF$_4$, and [Ni(*m*-stien)$_2$-(O_2N)]NO$_2$, each of which contains a chelated nitrite group, and the spectrum of the stilbenediamine complex is shown in Fig. 16. In addition to the "*d–d*" transitions, the complexes containing chelating nitrite groups also show a weak band centred at 23000 cm^{-1} and a stronger band at 27000 cm^{-1} each of which usually has considerable vibrational fine structure at low temperature. These were assigned to the spin-forbidden and spin-allowed $n \rightarrow \pi^*$ internal nitrite transitions. Since fine structure was only observed on the band at ~23000 cm^{-1} in complexes containing chelating nitrite groups

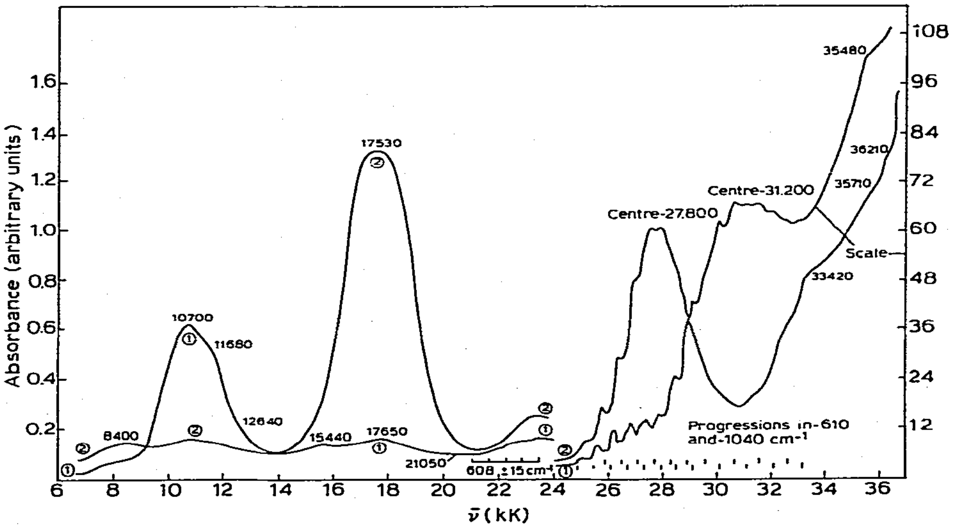


Fig. 16. Electronic spectrum of an arbitrary crystal face of [Ni(*m*-stien)$_2$(O_2N)]NO$_2$ with the electric vector along each extinction direction measured at 10 K. Note the change in absorbance scale at 24000 cm^{-1} [118].

it was suggested that this may prove to be a useful way of inferring the presence of a group of this kind in a nickel(II) complex.

The electronic spectra of a number of nickel(II) complexes containing bridging nitrite groups of various kinds have been described. The spectra of the compound $[N(CH_3)_4]Ni(NO_2)_3$ and a series of complexes of the type $Ni(diamine)(NO_2)_2$, all of which are thought to contain metal ions linked by (*NO*) nitrito bridges, all show peaks centred at ~ 12000 and ~ 20000 cm^{-1} characteristic of nickel(II) in a comparatively strong octahedral ligand field [52]. A similar spectrum occurs for the complex $[Ni(en)_2(NO_2)]X$, $X = ClO_4$ and BF_4 [53]. However, in view of the arguments presented above, it now seems likely that the peak at ~ 20000 cm^{-1} is probably non-"*d–d*" in origin. This is confirmed by the unusual spectra of a number of oligomeric complexes of general formula $Ni(L)_2(NO_2)_2 \cdot xC_6H_6$, where L is an aromatic amine and x may be 0, 1/3 or 1 [43,52]. These compounds exhibit a broad band centred at ~ 11000 cm^{-1}, and a pair of peaks at ~ 17000 and ~ 20000 cm^{-1}. Initially, it was postulated that the observation of two peaks in the visible region implies the presence of nickel ions in two different ligand environments, one having the metal bound to the nitrite groups solely via oxygen, and the other involving nitrogen-coordinated nitrite groups [44,52]. This was subsequently shown to be correct [43,44], in that in the trimer

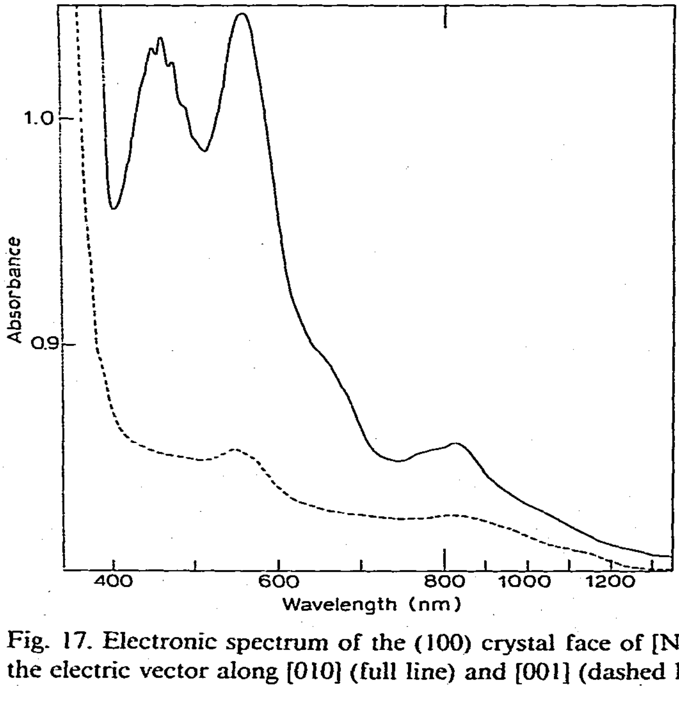


Fig. 17. Electronic spectrum of the (100) crystal face of $[Ni(4\text{-}mepy)_2(NO_2)_2]_2 \cdot 2\,C_6H_6$ with the electric vector along [010] (full line) and [001] (dashed line) measured at 7 K [43].

$[Ni(3\text{-mepy})_2(NO_2)_2]_3 \cdot C_6H_6$ the outer nickel(II) ions were found to be bound to nitrite groups solely via oxygen, while the central nickel is bonded to two nitrite nitrogen atoms (Fig. 7). However, it now seems that this correlation between the spectra and the presence of inequivalent nickel(II) ions is unwarranted, since a very similar spectrum is observed for the nitro complex *cis*-$[Ni(\mathit{NN}\text{-dimen})_2(\mathit{N}O_2)(H_2O)]ClO_4$ in which only one type of nickel(II) ion is present (Fig. 14) [116]. It therefore seems much more likely that the peak at ~20000 cm^{-1} in these polymers is a similar transition to that observed in nickel(II) complexes containing monodentate nitro groups, being probably a weak metal → nitrite π^* transition. The peak at ~17000 cm^{-1} is then assigned to the second spin-allowed transition of the nickel(II) ions bound to nitrite groups solely via oxygen, with the position of the corresponding band of the nickel bonded to nitrite nitrogen atoms remaining uncertain. The non-"*d–d*" origin of the band at ~20000 cm^{-1} is clearly seen in the low-temperature crystal spectrum of the dimer $[Ni(4\text{-mepy})_2(NO_2)_2]_2 \cdot 2\,C_6H_6$ [43], which shows well resolved vibrational progressions of energy ~600 cm^{-1} on this peak (Fig. 17), implying that the transition involves promotion of an electron into the nitrite π^* orbital. Similar arguments apply to the spectra of the series of pentamers of general formula $[Ni_5(\text{diamine})_5(NO_2)_8(OH)_2]$, some of which also show a pair of bands at ~17000 and ~20000 cm^{-1} [51].

(e) Copper(II)

Although the electronic spectra of a number of these is usually complicated by the presence of a highly distorted coordination geometry, the spectrum of the $Cu(NO_2)_6^{4-}$ ion in compounds containing a variety of different counter-cations has been described [124], including a single-crystal study of the complex $K_2BaCu(NO_2)_6$ [137]. In some of these, such as those formed by the alkali and alkaline-earth metals, the $Cu(NO_2)_6^{4-}$ ions have an elongated tetragonal geometry arranged in a ferrodistortive manner so that the long axes of the octahedra are parallel to one another [138]. In the salts formed by other cations, such as Pb^{2+}, the $Cu(NO_2)_6^{4-}$ units apparently exhibit a compressed coordination geometry, with four long and two short Cu–N bonds [139,140]. There has been considerable controversy over the nature of the bonding in these latter compounds, with some workers suggesting that they represent a true example of a copper complex having a compressed tetragonal geometry [141] and others maintaining that they contain a disordered arrangement of elongated $Cu(NO_2)_6^{4-}$ groups, occurring in an antiferrodistorted manner with the long and short axes alternating so as to give an overall appearance of a compressed tetragonal geometry [142]. This question is considered further in connection with the EPR spectra of the complexes, but it is clear that the electronic and IR spectra of the complexes differ only in such minor details as are commensurate with the variation in site symmetry and counter-cation [137,140,142]. In our opinion this tends to support the view that tetragonally elongated $Cu(NO_2)_6^{4-}$ units are present in both types of compound. The spectra of all the complexes show peaks at ~7000 and 15000 cm^{-1} which have been assigned to the "*d–d*" transitions $A_{1g}(d_{z^2}) \leftarrow B_{1g}(d_{x^2y^2})$ and a superposition of $E_g(d_{xz}, d_{yz}) \leftarrow B_{1g}(d_{x^2-y^2})$ and $B_{2g}(d_{xy}) \leftarrow {}^1B_{1g}(d_{x^2-y^2})$, respectively, with a further band occurring at ~20000 cm^{-1} which is probably charge transfer in origin. This assignment suggests a value of $\Delta_0 \simeq 12500$ cm^{-1} for the nitro group towards copper(II) [124], which is similar to that obtained in the analogous cobalt(II) and nickel(II) complexes.

The spectra of solid $K_3Cu(NO_2)_5$ [143], and of [*o*-cat]$Cu(NO_2)_4$ [33] in both the solid state and solution, have been reported. The former compound has a complicated crystal structure involving two different types of $Cu(NO_2)_5^{4-}$ units [34] and no attempt has been made to interpret the electronic spectrum quantitatively. The IR spectrum of solid [*o*-cat]$Cu(NO_2)_4$ suggests the presence of monodentate nitrito groups, probably of type (iii) with the second oxygen atom of each nitrite "semi-coordinated" to the metal. The electronic spectrum of the solid compound shows a broad peak centred at ~ 13000 cm^{-1}, this being typical of a copper(II) complex with a tetragonally distorted octahedral coordination geometry. It is interesting to note that solution in methyl cyanide produces a marked shift of this peak to higher energy, implying that the coordination geometry becomes more nearly planar in solution [33]. The polarized crystal spectrum of the complex $[Cu(bipy)_2(NO_2)]NO_3$ which contains a chelating nitrite ion, has been described [144], and interpreted in terms of a distorted octahedral ligand coordination geometry.

(f) Other metal ions

The electron-transfer spectra of compounds containing the hexanitrometallate ions $M(NO_2)_6^{3-}$, M = Co, Ir, Rh and $M(NO_2)_6^{4-}$, M = Fe, Co, Ni, Cu, have been discussed by Caulton and Fenske [119]. In all of these, a band at ~20000 cm^{-1} was assigned as a weak ligand → metal charge-transfer transition, with more intense peaks at 35000 and ~45000 cm^{-1} being assigned as metal → nitrite π^* and nitrite → metal transitions, respectively. More recently, Barnes et al. [120,136] have reported the electron-transfer spectra of $M(NO_2)_6^{4-}$, M = Cd, Hg, Pb, Fe, Co, Cu, Ni and $M(NO_2)_6^{3-}$, M = Ln, Ce, Bi, Co. Where the metal is neither easily oxidized nor reduced, e.g. Cd^{2+}, Y^{3+} or La^{3+}, the spectrum is essentially similar to that of $NaNO_2$, with a peak due to the spin-forbidden $n \rightarrow \pi^*$ nitrite transition being observed, centred at ~23000 cm^{-1}. When the metal is easily oxidized, e.g. Ce^{3+}, Bi^{3+} and Pb^{2+}, a peak is observed at 21000–23000 cm^{-1} which is assigned as a metal → nitrite π^* transition. For the hexanitro complexes of the transition metals these authors question the validity of the assignments proposed by Caulton and Fenske and conclude that it is at present impossible to be certain about the nature of the bands observed above ~20000 cm^{-1} in the spectra of these complexes. As already mentioned, work on mixed-ligand nitro complexes of nickel(II) suggests that for this metal ion the peak is probably due to a weak metal → nitrite π^* transition. It seems clear that in general further work on the spectra of these compounds is warranted, and in the view of the present authors it may well turn out that metal → ligand, ligand → metal and internal nitrite transitions all occur at comparatively low energy in transition metal nitro complexes, with the relative energy and intensity of these depending on the nature and oxidation state of the metal ion.

The electronic spectra of a number of amine complexes of Ir(III) involving monodentate nitro and nitrito groups have been discussed by Schmidtke [145], while the spectra of the nitro complexes $K_2Pt(NO_2)_4$ and $K_2Pt(NO_2)_6$ have been reported by Swihart and Mason [146].

(iii) Magnetic resonance measurements

The EPR spectra of a variety of compounds of the type $M_2M'Cu(NO_2)_6$ have been reported [137,140–142]. When M is an alkali metal and M′ an alkaline earth, the $Cu(NO_2)_6^{4-}$ groups exhibit tetragonally elongated geometries arranged in a ferrodistortive fashion, i.e. with the long bonds parallel to one another [138]. These compounds give rise to "normal" EPR spectra having g values $g_\parallel \approx 2.26$, $g_\perp \approx 2.06$ quite similar to other copper(II) complexes with four short and two long bond lengths [124]. When M = K, Rb or Cs and M′ = Pb, however, the complexes exhibit what is apparently a compressed tetragonal ligand coordination geometry, with two bonds significantly shorter than the other four [139]. This implies a $^2A_{1g}$ ground state for the copper(II) ion with the unpaired electron residing in the $3d_{z^2}$ orbital. The EPR spectra of these latter compounds yield the g values $g_\parallel \simeq 2.06$, $g_\perp \simeq 2.15$ and there has been considerable controversy over the interpretation of these. Harrowfield et al. [141] have suggested that these are consistent with a tetragonally compressed geometry, the deviation of $g_\parallel$ from the free electron value of 2 expected for a "pure" d_{z^2} ground state being due to vibronic mixing of the $d_{x^2-y^2}$ orbital into the ground-state wavefunction. Reinen, Friebel and co-workers [142], on the other hand, have proposed that these compounds contain tetragonally elongated $Cu(NO_2)_6^{4-}$ units arranged in an antiferrodistortive manner, i.e. with the long and short axes of neighbouring complexes being interchanged. The apparent axial symmetry of the g tensor

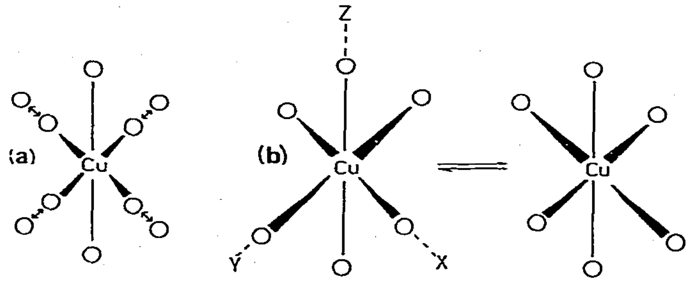


Fig. 18. Diagram illustrating two possible explanations of the unusual EPR parameters of $K_2PbCu(NO_2)_6$; (a) represents a vibronic mixing mechanism while (b) represents a rapid electron exchange between two tetragonally elongated molecules with orthogonal long axes.

is in this case due to the electron exchange between the neighbouring groups being more rapid than the EPR time scale. The two situations are illustrated schematically in Fig. 18. In order to explain the high value of $g_{\parallel}$ by a vibronic mixing of $d_{x^2-y^2}$ into the ground state, as proposed by Harrowfield et al. [141], the amplitude of the vibrations must be so large that the ground-state wavefunction in fact fluctuates between $d_{x^2-z^2}$ and $d_{y^2-z^2}$ (the axes being drawn as in Fig. 18). Such a vibration would be expected to have a low energy, so that this explanation is rendered extremely unlikely by the fact that the g values do not vary significantly with temperature [142]. It therefore seems more probable that, at least at room temperature and below, the complexes contain tetragonally elongated $Cu(NO_2)_6^{4-}$ units disordered in an antiferromagnetic arrangement. It is likely that at high temperatures some or all of these units undergo a dynamic fluctuation between the two forms, though the extent to which this occurs is at present not clear [124]. Recent neutron diffraction results are essentially in agreement with this interpretation [124,147]. The EPR spectrum of the $Co(NO_2)_6^{4-}$ ion has also been measured in several crystal lattices [123], and this ion exhibits g values commensurate with a tetragonally elongated geometry similar to that of the analogous copper complex. Again, in certain salts, the $Co(NO_2)_6^{4-}$ are apparently disordered in an antiferrodistortive arrangement, giving rise to an apparent compressed tetragonal structure when this occurs in two dimensions, or an apparently regular octahedral geometry when the disorder takes place in three dimensions [123,124].

The EPR spectrum of $K_3Cu(NO_2)_5$ has been reported [143], but the complicated crystal structure of this compound [34] precludes the interpretation of the g values in terms of metal–ligand bonding parameters. Single-crystal EPR spectra of the complexes $Cu(bipy)(NO_2)_2$ and $[Cu(bipy)_2(NO_2)]NO_3$ have been reported [144], and the molecular g values interpreted in terms of the distorted geometries of these complexes, which contain two and one unsymmetrically chelated nitrite groups, respectively. A single-crystal study of the EPR spectrum of the nitro complex $\mathrm{K_5Fe(CN)_5(NO_2)}$ has also been made and interpreted in terms of an elongated tetragonal ligand geometry, with the unpaired electron residing on the nitrite ligand [148].

The application of NMR spectroscopy to nitrite complexes has so far largely been limited to compounds of cobalt(III). The proton spectra of a variety of amine complexes containing nitro groups have been described [79,149–151] and the influence of stereochemistry on the spectra has been discussed. It would seem that while *cis* and *trans* geometrical isomers can be identified, little information can be gained on the nature of the metal–nitrite bond [151]. PMR spectra of acetylacetonato [127,128] and aminoacid [149] cobalt(III) nitro complexes have also been reported.

The ^{59}Co resonance of the $\mathrm{Co}(\mathit{N}\mathrm{O}_2)_6^{3-}$ ion in aqueous solution has been studied by Rose and Bryant [152] and Benedek et al. [153]; the latter workers reported the effects of variations in pressure and temperature on the spectrum. The ^{14}N spectrum of the nitro groups in $\mathrm{Co(NO_2)_6^{3-}}$ and several palladium(II) and platinum(II) complexes have been studied by Bramley et al. [154], who found a significant shift to high frequency compared with the free ion. This has since been questioned by Rose and Bryant [152], who have shown that the $\mathrm{Co}(\mathit{N}\mathrm{O}_2)_6^{3-}$ ion decomposes slowly in aqueous solution to produce $\mathrm{NO_3^-}$ and a cobalt(II) species, making the interpretation of the NMR spectrum difficult. So far, it is not known how the ^{14}N and ^{17}O resonance frequencies of the nitrite alter when this ligand is coordinated to a metal via oxygen. This would be of interest as it might provide information on the nature of the metal–ligand bond complementary to that obtained from the study of the electronic spectra of complexes, as well as providing a further means of distinguishing between the different types of nitrite coordination.

(iv) Mössbauer spectroscopy

The spectra of the series of compounds $\mathrm{A_2PbFe}(\mathit{N}\mathrm{O}_2)_6$, A = K, Tl, Rb and Cs, have been studied by Pebler et al. [155] who noted a dependence of the isomer shift on the probable Fe–N bond distance. These workers concluded that the nitro group is both a weaker σ-donor and π-acceptor than the cyanide ligand, this being in agreement with the results of a study of the Mössbauer spectrum of $\mathrm{K_2CaFe}(\mathit{N}\mathrm{O}_2)_6$ by Sano and Kono [156] who concluded that $\mathit{N}\mathrm{O}_2^-$ lies between $\mathrm{CN^-}$ and $\mathrm{NCS^-}$ in π-bonding ability.

(v) Magnetic susceptibility measurements

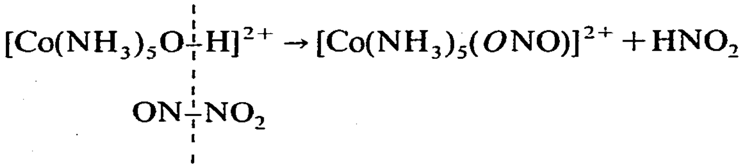
The room-temperature magnetic moments of a range of high-spin complexes of cobalt(II) of general formula $\mathrm{M(L)_2}(\mathit{O}_2\mathrm{N})_2$ have been reported, where L is a substituted aromatic amine [23], an amine oxide, or $(C_6H_5)_3PO$ and $(C_6H_5)_3AsO$ [42], and the nitrite groups chelate, possibly unsymmetrically. These compounds have μ_{eff} ranging from 4.4 to 5.0 Bohr Magnetons, consistent with the highly distorted ligand coordination geometry proposed for these compounds on the basis of their electronic spectra. The magnetic moments of a number of similar high-spin nickel(II) complexes of formula $Ni(L)_2(NO_2)_2$ and $Ni(diamine)(NO_2)_2$, where L is a substituted aromatic amine and diamine a heavily substituted ethylenediamine have also been reported [42]. These compounds also contain chelating nitrite ions, and the magnetic moments of $\mu_{eff} \approx 3.3$ Bohr Magnetons imply a distorted octahedral coordination geometry about the nickel(II) ion.

The temperature dependence of the magnetic susceptibilities of several polymeric nickel(II) complexes containing bridging nitrite groups of various kinds have been investigated over the temperature range 300–390 K [52]. These compounds all show evidence of an antiferromagnetic ordering at low temperatures. In the case of the trimer $[Ni(3\text{-mepy})_2(NO_2)_2]_3C_6H_6$, which contains nickel(II) ions linked by one type (*NO*) and one (*O*) nitrito bridge (Fig. 7), the magnetic interactions were interpreted in terms of a superexchange mechanism in which adjacent metal ions are coupled with an exchange integral $J = -11$ cm^{-1}. In the compound $[Ni(en)_2(NO_2)]ClO_4$, which contains linear chains of nickel(II) ions linked by type (vii) (*NO*) bridges, the temperature dependence of the magnetic susceptibility can be explained in terms of the Heisenberg model of antiferromagnetic coupling with a value of $J = -18$ cm^{-1} and this is also rationalized in terms of a superexchange mechanism. It is clear that the presence of nitrite bridges can be expected to give rise to comparatively large magnetic interactions between metal ions, and as each type of bridge is characterized by a specific metal–metal distance and a different arrangement of ligand orbitals connecting the metal ions it seems likely that when the measurement of magnetic properties at very low temperatures becomes a routine method of investigation, the study of polymeric nitrite complexes will provide a valuable insight into the nature of superexchange mechanisms, as well as possibly providing a means of distinguishing between the different kinds of nitrite bridge.

F. FACTORS INFLUENCING THE MANNER OF COORDINATION OF THE NITRITE LIGAND

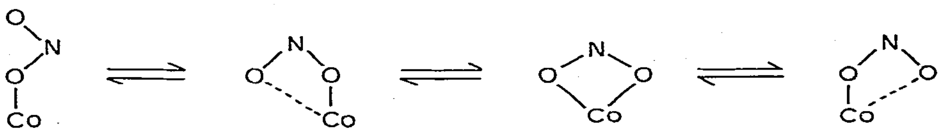
(i) Kinetic effects

The isolation of the thermodynamically unstable nitrito complex $[Co(NH_3)_5(ONO)]Cl_2$ provided the first known example of linkage isomerism, and the mechanisms whereby this compound is formed, and subsequently rearranges to produce the more stable nitro isomer have been the subject of several investigations [157–159]. The elegant experiments of Basolo et al. [157] involving isotopically labelled oxygen have shown that the cobalt nitrito complex is in fact formed by attack of N_2O_3 on an intermediate hydroxo complex



$$\begin{array}{l}[\mathrm{Co(NH_3)_5O}\,\vdots\,\mathrm{H}]^{2+} \rightarrow [\mathrm{Co(NH_3)_5}(\mathit{O}\mathrm{NO})]^{2+} + \mathrm{HNO_2} \\ \qquad\quad \mathrm{ON}\,\vdots\,\mathrm{NO_2}\end{array}$$

The nitrito complex thus forms by the effective addition of NO to a coordinated hydroxyl group and subsequently undergoes an intramolecular rearrangement to form the more stable nitro isomer [160–162]. The kinetics of this rearrangement have been studied by several workers and thermodynamic parameters for the reaction have been derived [161,162]. The complexes $[M(NH_3)_5(ONO)]^{2+}$, M = Co, Rh, Ir, have also been observed to undergo an intramolecular nitrito-to-nitro rearrangement which is catalysed by base, and these reactions have been studied in detail by Jackson et al. [187]. As a result of ^{18}O tracer experiments, these workers also made the interesting observation that the oxygen atoms in $[Co(NH_3)_5(ONO)]^{2+}$ interchange more rapidly than the nitrito-to-nitro conversion. Possibly, this exchange occurs via a comparatively low-energy pathway involving a nitrito linkage with the non-bonded oxygen *cis* to the metal; this might well allow the "scrambling" of the nitrite oxygen atoms via a formally seven-coordinate intermediate involving a chelating nitrite



The nitro isomer of $[Co(NH_3)_5(NO_2)]^{2+}$ is expected to have a smaller volume than the nitrito form, and this has been confirmed by studies of the effect of pressure on the reaction kinetics of the nitrito-to-nitro interconversion [186]. It is interesting to note that the position of the equilibrium can be reversed by exposing the complex to UV light [159,162]. The reason for this is not clear, though it presumably means that nitrito coordination is preferred in a fairly long-lived excited state. The kinetics of formation of the nitrito isomer of several complexes of cobalt(III) with ethylenediamine have also been studied [158], as have the formation and subsequent rearrangement of similar complexes of Cr(III), Pt(IV), Ir(III) and Rh(III) [163]. With the exception of the chromium complex, for which the nitrito complex is quite stable, these all show behaviour rather similar to that of the $[Co(NH_3)_5(NO_2)]^{2+}$ ion, suggesting that in every other case the thermodynamically stable form of monodentate nitrite coordination is via nitrogen, and that the metastable nitrito isomer can only be isolated because of the comparatively inert nature of the complexes formed by Co(III), Rh(III), Ir(III) and Pt(IV). The kinetics of the exchange of the nitro groups in *trans*-bis(2-amino-2-methyl-3-butanoneoximato)dinitrocobalt(III) with nitrite in aqueous solution has been studied by Murmann and Rahmoeller [188], who concluded that the reaction may possibly proceed via a higher-energy nitrito isomer.

(ii) Steric effects

It has been suggested that steric crowding in a complex may influence the manner of coordination adopted by several ligands [164], including the nitrite ion [22,42,88]. It is hard to prove a conjecture of this kind but perhaps the best circumstantial evidence is provided by a comparison of the structures observed for a range of nitrite complexes formed by the same metal with ligands which are expected to differ primarily in their steric characteristics. To date, the most comprehensive information of this kind concerns the complexes formed by nickel(II) nitrite with a variety of amine ligands, and the structures observed for representative examples of these are listed in Table 5.

Probably the clearest evidence that the manner of nitrite bonding can be influenced by the steric nature of neighbouring ligands occurs for monodentate nitrite coordination to nickel(II). When this is compared in the series of complexes of general formula $Ni(diamine)_2(NO_2)_2$ formed by substituted ethylenediamines (Table 5) it is apparent that there is a general trend for the nitrite to coordinate via nitrogen when little interligand steric crowding is expected, but via oxygen when the ligands carry bulky substituents. Monodentate nitrito coordination also occurs in a series of complexes of general formula $Ni(L)_4(\mathit{O}NO)_2$, where L is one of a number of aromatic amines, and significant steric crowding is expected in these also. The nitrito coordination is apparently always of the *trans* type [Fig. 1(ii)]. As crystal structure determinations have been carried out on a number of these compounds it is possible to compare the disposition of the nitrite groups with respect to a variety of other ligands having different steric properties. The ways in which nitrito coordination might be expected to reduce repulsive interactions with neighbouring ligands, when compared with nitro coordination, are shown schematically in Fig. 19. For a monodentate nitrite group, the main repulsive interactions with neighbouring ligands are expected to involve the two non-bonded oxygen atoms in a nitro complex and the non-bonded nitrogen

TABLE 5

Nitrite coordination observed in nickel(II) nitrite complexes of various diamines

Compound	Coordination type	State	Evidence	Ref.
$\mathrm{Ni(en)_2(}N\mathrm{O_2)_2}$	*trans* Nitro	Solid	X-Ray	13
$\mathrm{[Ni(en)_2(}O_2\mathrm{N)]NO_2}$ [a]	Chelating	Solid, high temperature	IR	171 [a]
$\mathrm{[Ni(en)_2(}N\mathrm{O_2)_2]\cdot H_2O}$	*cis* Nitro	Solid	X-Ray	15
$\mathrm{[Ni(}NN'\mathrm{\text{-}dimen)_2(}N\mathrm{O_2)_2]\cdot H_2O}$	*trans* Nitro	Solid	X-ray	14
$\mathrm{Ni(}NN\mathrm{\text{-}dimen)_2(}O\mathrm{NO)_2}$	*trans* Nitrito	Solid, solution in $\mathrm{CHCl_3}$ in equilibrium with nitro form	X-Ray, electronic spectrum	26, 14, 88
$\mathrm{Ni(}NN\mathrm{\text{-}dimen)_2(}N\mathrm{O_2)_2}$	Nitro	Solution in $\mathrm{CHCl_3}$ in equilibrium with nitrito form	Electronic spectrum	88
$\mathrm{Ni(}NN\mathrm{\text{-}dieen)_2(}O\mathrm{NO)_2}$	*trans* Nitrito	Solid	IR and electronic spectrum	118, 22
$\mathrm{[Ni(}NN'\mathrm{\text{-}dieen)_2(}O_2\mathrm{N)]NO_2}$	Chelating	Solid	X-ray	31
$\mathrm{Ni(}NN'\mathrm{\text{-}dieen)_2(}N\mathrm{O_2)_2}$	Nitro	Solid, low-temperature solution in $\mathrm{CHCl_3}$ in equilibrium with nitro form	Electronic spectrum	170, 88
$\mathrm{Ni(}NN'\mathrm{\text{-}dieen)_2(}O\mathrm{NO)_2}$	Nitrito	Solution in $\mathrm{CHCl_3}$ in equilibrium with nitro form	Electronic spectrum	88
$\mathrm{[Ni(}m\mathrm{\text{-}stien)_2(}O_2\mathrm{N)]X}$ $\mathrm{X=NO_2^-, Cl^-, ClO_4^-}$	Chelating	Solid	X-Ray	30
$\mathrm{[Ni(}NN'\mathrm{\text{-}dieen)_2(}O_2\mathrm{N)]BF_4}$	Chelating	Solid	X-Ray	40
$\mathrm{[Ni(en)_2(}O_2\mathrm{N)]X}$ $\mathrm{X=Cl^-, Br^-, I^-, NO_3^-}$	Chelating	Solid	X-Ray	8, 15
$\mathrm{[Ni(en)_2(}ON\mathrm{O)]X}$	Type (v) (NO) bridges	Solid	X-ray	38, 53

[a] This interpretation of the type of coordination present in the high-temperature, blue form of $\mathrm{Ni(en)_2(NO_2)_2}$, which differs from that of the original authors, is based upon the reported IR spectrum; see section G.

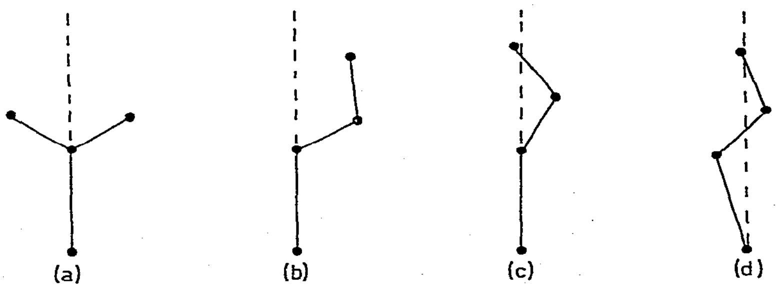


Fig. 19. Schematic diagram showing how monodentate nitrito coordination may reduce interligand steric interaction compared with nitro coordination; (a) represents nitro coordination, (b) nitrito coordination in the absence of any steric constraints, (c) nitrito coordination but with the angle MON increased from 120 to 150° and (d) nitrito coordination but with the M–O bond direction displaced by 10° from the octahedral axis.

atom in a nitrito complex. It can be seen that if a nitro group is replaced by a nitrito group with the metal–nitrite bond being in each case orthogonal to the plane defined by the in-plane ligand atoms and the angle MON being ~ 120°, then the steric interaction with neighbouring ligand atoms is not in fact expected to decrease significantly (though, of course, only one such interaction occurs for a nitrito complex compared with two for a nitro complex). However, in the case of nitrito coordination steric interference with neighbouring ligands may be reduced either by a tilting of the nitrite so as to increase the angle NiON [Fig. 19(c)], or by a displacement of the whole ligand so that the Ni–O vector is no longer orthogonal to the NiL_4 plane [Fig. 19(d)]. An examination of the structural data available for nickel nitrito complexes suggests that in the complex *trans*-Ni(*NN*-dimen)$_2$(*O*NO)$_2$ [14] the coordination is of the type shown in Fig. 19(b). The only evidence for the presence of significant steric crowding in this molecule is provided by the anomalously long Ni–N bond distances to the substituted amine nitrogen atoms [14]. In [Ni(py)$_4$(*O*NO)$_2$] · 2 py and [Ni(4-mepy)$_4$(*O*NO)$_2$] [28], however, the nitrito coordination is of the type illustrated in Fig. 19(c), with the Ni–O bonds remaining essentially orthogonal to the plane defined by the Ni^{2+} ion and the amine nitrogen atoms, but with the angle NiON increased from ~ 120 to ~ 150°. In the complex Ni(2-meim)$_4$(*O*NO)$_2$ [29], on the other hand, nitrito coordination of the type shown in Fig. 19(d) is observed. One of the Ni–O bond distances in this molecule is abnormally long (2.25 Å), and both Ni–O bond vectors are displaced by ~ 11° from the normal to the plane defined by the coordinated amine nitrogen atoms, the sense of the displacement being such as to minimize the contact between the nitrite nitrogen atoms and the amine ligands. A similar displacement of the nitrito groups is observed in the complex Ni(pyr)$_4$(*O*NO)$_2$ [28] though here the situation is complicated by the fact that the distortion may be stabilized by the formation of hydrogen bonds involving the amine NH groups. In all of these complexes non-bonding contacts involving the nitrite groups are observed at about the van der Waals limit. The evidence thus suggests that steric crowding increases along the series $\mathrm{Ni}(NN\text{-dimen})_2(O\mathrm{NO})_2 < \mathrm{Ni(py)}_4(O\mathrm{NO})_2 < \mathrm{Ni(2\text{-}meim)}_4(O\mathrm{NO})_2$ and in connection with this it is interesting to note that whereas $\mathrm{Ni}(NN\text{-dimen})_2(O\mathrm{NO})_2$ is a nitrito complex, the corresponding complex formed by the symmetrically substituted diamine, $[\mathrm{Ni}(NN'\text{-dimen})_2(N\mathrm{O}_2)_2]\cdot \mathrm{H_2O}$ is, in fact, a nitro complex [14]. The molecular structures of these two complexes are shown in Figs. 3(a) and (b). The major interligand steric crowding in these complexes is expected to involve the amine substituents occupying axial positions of the chelate rings and in both compounds two methyl substituents are of this type. However, while in $\mathrm{Ni}(NN\text{-dimen})_2(O\mathrm{NO})_2$ each chelate ring carries one axial substituent, in $[\mathrm{Ni}(NN'\text{-dimen})_2(N\mathrm{O}_2)_2\cdot \mathrm{H_2O}$ both substituents of this kind are on one of the chelate rings. In both molecules the planes of the nitrite groups are disposed so that the steric interactions with the amine substituents are minimized, this resulting in the planes of the nitrite groups being parallel in $\mathrm{Ni}(NN\text{-dimen})_2(O\mathrm{NO})_2$, but orthogonal in $[\mathrm{Ni}(NN'\text{-dimen})_2(N\mathrm{O}_2)_2]\cdot \mathrm{H_2O}$. It would thus seem that the overall geometries of these molecules are strongly influenced by interligand repulsions, with the factors favouring nitro and nitrito coordination being about equally balanced. In agreement with this, spectral evidence suggests that upon solution in several organic solvents the compound $\mathrm{Ni}(NN\text{-dimen})_2(O\mathrm{NO})_2$ undergoes a dynamic equilibrium between nitro and nitrito isomeric forms [88,165,166]. This behaviour is discussed further in section G. It is also noteworthy that when one nitrite group in this complex is replaced by a water molecule, as occurs in the compound *cis*-$[\mathrm{Ni}(NN\text{-dimen})_2(N\mathrm{O}_2)(\mathrm{H_2O})]\mathrm{ClO_4}$ [116], a nitro complex results. This is in agreement with the above arguments, since the replacement of a nitrite group by the smaller water molecule should cause a lessening of the interligand steric crowding.

As yet, insufficient systematic evidence is available to allow the assessment of the influence of steric effects on the manner of monodentate nitrite coordination in complexes involving metal ions other than nickel(II). A range of nitrito complexes of the type $\mathrm{Co(diamine)}_2(O\mathrm{NO})_2$ and $\mathrm{Co(L)}_4(O\mathrm{NO})_2$ analogous to the above mentioned nickel(II) compounds have been reported, but it was found that when amines which yield stable nitro complexes with nickel(II) were used, no stable cobalt(II) complexes were formed [23]. It is possible that while steric effects stabilize the oxygen coordination of the nitrite groups in these cobalt(II) nitrito complexes, the nitro complexes formed with amines bearing less bulky substituents are unstable, at least under the experimental conditions used. This is surprising, as the stability of the hexanitrocobaltate(II) ion is well established, and a further investigation of these mixed-ligand cobalt(II) nitrite complexes would seem to be warranted. It would also be interesting to see whether the thermodynamically unstable nitrito complexes formed by the metal ions Co(III), Rh(III), Ir(III) and Pt(IV) can be stabilized by the use of bulky ligands similar to those which apparently have this effect in nickel(II) nitrite complexes.

The influence of steric factors upon bidentate nitrite coordination is less well defined than is the case for monodentate coordination. Again, the most comprehensive data available concern complexes of nickel(II). In a series of octahedral complexes of general formula $Ni(diamine)(NO_2)_2$ Goodgame et al. have suggested on the basis of spectral and magnetic evidence that the complexes formed by ethylenediamine and mono-*N*-substituted ethylenediamines involve (*NO*) nitrite bridges, while the complexes with tetra *N*-substituted amines contain chelating nitrite groups [42,52]. It has also been observed that in complexes of the type $Ni(L)_2(NO_2)_2$, where L represents an aromatic amine, monomeric complexes involving chelating nitrite groups occur with amines likely to cause steric crowding, such as 2-methylpyridine and quinoline, while amines such as isoquinoline and 3-methylpyridine form polymeric complexes [42,52]. It might be inferred from this that (*NO*) bridging is the "preferred" method of bidentate nitrite coordination to nickel(II), with chelation only occurring when the presence of bulky ligands prevents the metal ions from approaching closely enough to allow the formation of polymers. An examination of the nitrite bonding in the complexes of stereochemistry $[Ni(diamine)_2(NO_2)]X$, where X is an uncoordinated anion, shows that this interpretation is too simplistic (Table 5). It is true that the complexes of this type formed by ethylenediamine where $X = ClO_4^-$ and BF_4^- contain linear chains of nickel(II) ions linked by type (v) (*NO*) nitrito bridges (Fig. 9) [38,53]. However, the analogous compounds where $X = Cl^-$, Br^- or NO_3^- contain chelating nitrite groups [8,9], and steric crowding in the $[Ni(en)_2(O_2N)]^+$ ion must be minimal. Chelating nitrites are also present in the complexes $[Ni(NN'\text{-dieen})_2(NO_2)]X$, $X = NO_2^-$ [31] and BF_4^- [40], $[Ni(m\text{-stien})_2(NO_2)]X$, $X = NO_2^-$, Cl^- and ClO_4^- [30], $[Ni(bipy)_2(NO_2)]NO_3$ [167] and in the compound $[Ni(2\text{-meim})_4(NO_2)]NO_3 \cdot \frac{1}{2}CH_3OH$ [29].

It has been suggested that packing considerations may influence the type of nitrite coordination adopted in a series of novel polymeric complexes of general formula $Ni(L)_2(NO_2)_2$, where L is 3- or 4-methylpyridine or isoquinoline [44,52]. Spectroscopic evidence implies that the nickel(II) ions in these compounds are linked by both (*NO*) and (*O*) nitrite bridges. Three compounds of this type have been obtained from benzene solution, each containing clathrated solvent: $[Ni(L)_2(NO_2)]_3 \cdot C_6H_6$, L = py or 3-mepy, and

$[Ni(4\text{-mepy})_2(NO_2)_2]_2 \cdot 2C_6H_6$. The geometry of the trimer formed by 3-methylpyridine is shown in Fig. 7, and it seems likely that the analogous pyridine complex has a similar structure. The dimer formed by 3-methylpyridine has a somewhat similar geometry [see section C(vii)]. In each case the planes of the *trans* aromatic amine molecules are approximately parallel to one another, and orthogonal to the metal–metal direction. The five-membered ring formed by the two bridging nitrite groups produces a Ni–Ni separation (~ 3.4 Å) which just equals the van der Waals separation between two parallel aromatic ring systems, and it was suggested [44] that this may be an important factor helping to stabilize the bridging arrangement of the nitrite groups in this series of compounds.

Steric factors also apparently influence the nature of the nitrite bridges present in a series of unusual pentamers of general formula $Ni_5(\text{diamine})_4(NO_2)_8(OH)_2$ [51]. The structure of the complex formed by ethylenediamine is shown in Fig. 8. Each pentamer contains a planar, centrosymmetric array of five nickel(II) ions, the outer four being linked to the central metal by four type (iv), (*NO*)-bridging nitrito groups and two three-coordinate bridging hydroxide ions. Each outer pair of nickel(II) ions are also linked by two bridging nitrito groups, with the four chelating diamine ligands occupying the coordination sites at the apices of the oligomer. In the ethylenediamine complex each pair of outer nickel(II) ions are joined by two (*NO*) nitrito bridges and the central nickel is bonded to the oxygen atoms of the bridging nitrito groups. Spectral evidence suggests that the complex formed by *N*-methylethylenediamine has a similar geometry. The complexes formed by *NN'*-dimethylethylenediamine and *NN'*-diethylethylenediamine have very similar structures, except that one of the nitrite groups bridging each pair of outer nickel(II) ions is disordered, this producing a slightly different electronic spectrum from that observed for the above mentioned compounds. The nitrite bridging in the pentamer formed by *NN*-dimethylethylenediamine differs from that in the other four complexes in two respects. Firstly, the arrangement of the (*NO*) nitrito bridges linking the central nickel to the outer four metal ions is reversed, so that the central nickel is bonded to these groups via nitrogen rather than oxygen. Secondly, one of the two nitrito bridges connecting each pair of outer nickel ions occurs via a single oxygen atom, rather than nitrogen and oxygen. It seems highly probable that these changes are caused by the more stringent steric requirements of the amine substituents in the latter complex. Whereas in $Ni_5(NN'\text{-dieen})_4(NO_2)_8(OH)_2$ both substituents on each amine are found to occupy equatorial sites of the chelate rings, in $Ni_5(NN\text{-dimen})_4(NO_2)_8(OH)_2$ one substituent on each amine must occupy an axial site, hence bringing it into comparatively close contact with the nitrite ligands. It seems likely that this causes the nitrite groups bridging to the central nickel to change from nitrogen to oxygen coordination, as far as the nickel ions bonded to the amine ligands are concerned. This is, in fact, exactly analogous to the switch from monodentate nitro to nitrito coordination used to rationalise the fact that $\mathrm{Ni}(NN\text{-dimen})_2(O\mathrm{NO})_2$ is a nitrito complex, while compounds with less heavily substituted amines are often nitro complexes [22,88]. Similarly, the (*O*) nitrito bridges which occur in conjunction with the asymmetrically substituted diamine probably produce less steric crowding in the molecule than the (*NO*) nitrito bridges present in the pentamers formed by the other amines.

All in all, it seems likely that chelation is the "preferred" method of nitrite coordination in nickel(II) complexes involving ligands of such bulk that the formation of polymeric species is impossible. Where restrictions of this kind do not apply it appears that chelation, and (*O*) and (*NO*) nitrite bridges all occur fairly frequently, and the actual structure appears to depend upon the steric requirements of the other ligands in the complex, or the nature of any counter-anions which are present in the lattice.

A further example of the apparent effect of interligand interactions upon the manner of nitrite coordination may be inferred from the types of bonding present in the tetranitrite ions $\mathrm{M(NO_2)_4^{2-}}$, M = Mn, Co, Zn, Cd and Hg [33]. In each of these ions the nitrites coordinate via oxygen, but while this occurs by approximately symmetrical chelation in the Mn, Cd and Hg complexes, essentially monodentate nitrito groups are present in the Zn and Co compounds. The structure of the $\mathrm{Cd(NO_2)_4^{2-}}$ ion [45] is shown in Fig. 4(a); the $\mathrm{Hg(NO_2)_4^{2-}}$ is known to have an analogous geometry [46] and the IR spectrum of the $\mathrm{Mn(NO_2)_4^{2-}}$ ion is very similar to those of the other two complexes, (Fig. 10). The geometry of the $\mathrm{Zn(NO_2)_4^{2-}}$ ion [45] is illustrated in Fig. 4(b), from which it may be seen that the nitrito groups adopt the unusual type (iii) *cis* nitrito conformation, which may be considered to be a highly asymmetric form of chelation. Infrared and electronic spectra suggest a similar geometry for the cobalt(II) complex [33]. It seems likely that the difference between the modes of coordination of the nitrites in the two groups of compounds is related to the size of the metal ion. The ionic radii of zinc(II) and cobalt(II) (0.69 and 0.82 Å, respectively) are significantly smaller than those of manganese(II), cadmium(II) and Hg(II) (0.91, 1.03 and 0.93 Å). It seems plausible that for the former pair of metal ions interligand repulsions make a geometry with eight equivalent metal–oxygen bonds relatively unstable with respect to one with four short, and four much longer bond lengths. With the three larger metal ions, however, interligand repulsions are expected to be less important and the geometry with eight essentially equivalent metal–ligand bond distances is adopted.

(iii) Electronic effects

The nature of the metal–nitrite bonding might possibly be affected by the electronic structure of either the metal ion or of the other ligands in a complex. There is as yet no clear cut evidence that the electronic structure of the other ligands has any effect upon the nature of the metal–nitrite bond. However, a comparison of the metal–nitrite coordination in complexes having a similar stoichiometry formed by different metal ions shows that the electronic structure of the metal can have a pronounced effect upon the mode of bonding adopted by the nitrite. Thus, while it is clear that the thermodynamically stable form of monodentate nitrite coordination to cobalt(III) is via nitrogen, analogous chromium(III) compounds are invariably nitrito complexes. The tendency for the nitrite to coordinate via nitrogen when bound to cobalt(III) is further shown by the fact that when nitrite bridges are formed between two cobalt(III) ions these are always via nitrogen and oxygen. As yet, no chromium(III) complexes containing bridging nitrite groups have been investigated, and it will be interesting to see whether the tendency for the nitrite to bind via oxygen to this metal is also shown for bidentate coordination. If this is the case, it may be that examples of nitrite groups bridged via two oxygen atoms [Fig. 1(vii)] will be found in polymeric chromium(III) nitrite complexes. In this context it may be noted that the nitrite ion bears a formal resemblance to the acetate group, which is well known to bridge in this fashion [168].

Another example of the influence of the electronic structure of the metal upon the nature of the nitrite coordination is provided by a comparison of analogous nickel(II) and zinc(II) complexes. Whereas the compound $Ni(en)_2(NO_2)_2$ is a nitro complex [14], the analogous zinc(II) complex $[Zn(en)_2(NO_2)]NO_2$ contains one chelating and one ionic nitrite ion [27]. It seems unlikely that ligand–ligand repulsions are responsible for the chelation of the nitrite in the latter compound, since the ionic radius of the zinc(II) is marginally greater than that of nickel(II). It is also noteworthy that whereas the compound $[Ni(en)_2(NO_2)]ClO_4$ contains nitrite groups bridging via nitrogen and oxygen the corresponding zinc(II) complex adopts a structure in which the nitrite ion chelates [38]. However, it must be remembered that the complexes $[Ni(en)_2(NO_2)]X$, $X = Cl^-$, Br^- and NO_3^- also contain chelating nitrite groups [8,9]. In fact, as with chromium(III), all known nitrite complexes of zinc(II) involve groups which are coordinated solely via oxygen, implying that this is the "preferred" method of nitrite coordination to this metal ion.

The influence of the nature of the metal ion on nitrite coordination is also shown by a comparison of the type of metal–nitrite bond found in various tetranitrite complexes. The species $M(NO_2)_4^{2-}$, M = Mn, Co, Cu, Zn, Cd and Hg all contain nitrite ions bonded via oxygen, either by monodentate or bidentate coordination [33]. In marked contrast, the compounds $K_2Pd(NO_2)_4$ and $K_2Pt(NO_2)_4$ are both planar nitro complexes [16]. This clearly reflects the tendency of these latter metal ions to form four strong, comparatively covalent bonds in a square-planar arrangement. It is interesting to note that the analogous complex of copper(II) contains nitrito groups [33], probably in a *cis* type arrangement, [Fig. 1(iii)], since this metal ion also shows a marked tendency to form complexes with a planar rather than a tetrahedral geometry. It seems likely that nitrito coordination is adopted in the copper(II) complex because this mode of coordination readily allows the formation of weak bonds in the axial position. These are a general feature of the d^9 electron configuration, but not of the low-spin d^8 electron configuration of the two heavier metals. It would be of some interest to learn whether the $Ni(NO_2)_4^{2-}$ ion adopts an essentially tetrahedral geometry involving nitrito coordination, as is the case for the $Co(NO_2)_4^{2-}$ ion, or is a low-spin planar nitro complex similar to $Pd(NO_2)_4^{2-}$ and $Pt(NO_2)_4^{2-}$. However, so far attempts to prepare a compound containing the nickel tetranitrite ion have failed [33].

The effect which the nature of the metal ion can have upon the characteristics of the nitrite coordination is well illustrated by a comparison of the geometries of the three molecules M(*NNN'N'*-tetmen)$(NO_2)_2$, M = Ni [38], Cu [36], Zn [38]. These complexes crystallize with isomorphous unit cells, but differ in the details of their geometry, as is indicated by the schematic diagrams shown in Fig. 5. As interligand interactions seem relatively unimportant in these molecules, the differences in stereochemistry are apparently related to the electronic structure of the metal ions. The geometry of the nickel complex is as close to that of a regular octahedron as the small "bite" of the chelating nitrite ligands will allow. In the analogous zinc complex, on the other hand, the chelation of the nitrite ligands is highly asymmetric, and it is interesting to note that if only the amine nitrogen atoms and the two closer, *trans* nitrite oxygen atoms are considered, these form a highly distorted tetrahedral geometry about the metal. The metal–ligand bond lengths in the copper(II) complex are rather similar to those in the zinc compound, the chelation of the nitrite groups being even more asymmetric. However, in the copper(II) complex it is the *trans* rather than the *cis* Cu–O bonds which are long, and it seems clear that in Cu(*NNN'N'*-tetmen)$(NO_2)_2$ the ligand geometry is best regarded as an essentially square-planar arrangement, with two semi-coordinated nitrite oxygen atoms occupying axial bonding sites. It seems likely that geometries of the nickel(II) and copper(II) complexes may each be influenced by the spatial distribution of the half-filled *d* orbitals, while possibly the tendency of the zinc(II) complex towards the adoption of a tetrahedral ligand arrangement may reflect the influence of the bonding requirements of the metal 4*s* and 4*p* orbitals upon the geometry of the complex.

G. LINKAGE ISOMERISM IN NITRITE COMPLEXES

The best known examples of this kind of isomerism are the nitro and nitrito monodentate linkage isomers formed by cobalt(III), rhodium(III), iridium(III) and platinum(IV). In all of the complexes so far studied, the nitrito isomer is unstable, and is only formed because of the unusual reaction kinetics and relatively inert nature of the complexes formed by these four metal ions [see section F(i)] [163]. In each case, the nitrito form changes virtually completely within a matter of hours or days into the more stable nitro form, although the procedure can be reversed by exposure to UV radiation [159,162]. The effect of pressure upon the nitro → nitrito conversion has been studied [186], and it was concluded that the nitro isomer has a smaller effective volume than the nitrito form {69.4 ± 0.1 cm^3 mol^{-1} as compared with 82.3 ± 1.4 cm^3 mol^{-1} for the ion $[\mathrm{Co(NH_3)_5}(O\mathrm{NO})]^{2+}$}.

The existence of linkage isomers involving monodentate nitro and nitrito coordination has also been postulated for several nickel(II) nitrite amine complexes, with the two molecular forms in these cases having a comparable thermodynamic stability [88,169–171]. When the solid compounds Ni(*NN*-dimen)$_2$(NO$_2$)$_2$ and Ni(*NN'*-dieen)$_2$(NO$_2$)$_2$, each of which is blue-green in colour, are dissolved in inert solvents such as benzene or chloroform, a reddish purple solution results. The electronic spectrum of these solutions shows a well resolved band centred at 20000 cm^{-1}, the intensity of which varies as a function of temperature [88,172]. The temperature dependence of the spectrum of Ni(*NN'*-dieen)$_2$(NO$_2$)$_2$ in chloroform has been studied by Goodgame and Hitchman [88], and more recently by Alexander and Holper [172], and interpreted in terms of an equilibrium of the form

$$\mathrm{Ni(diamine)_2}(N\mathrm{O_2})_2 \rightleftharpoons \mathrm{Ni(diamine)_2}(O\mathrm{NO})_2$$

with the concentration of the nitrito form increasing at higher temperatures. The following parameters were derived [172] for the conversion of the nitro to nitrito isomer

$$\Delta H = -4.4 \pm 1.0\ \mathrm{kJ\ mol^{-1}}, \quad \Delta S = -20 \pm 3\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Similar values were obtained for the complex Ni(*NN*-dimen)$_2$(NO$_2$)$_2$ [172]. These values are consistent with the bond enthalpy of the nitro isomer being somewhat greater in magnitude than that of the nitrito form, but with the latter isomer having a greater freedom of ligand movement. This is in agreement with the general ideas concerning the balance between electronic and steric factors as related to nitrite coordination to nickel(II) outlined in section F(ii). The effect of pressure on the above equilibrium has been reported by Sinn [165] and Alexander and Holper [172] who found that an increase in pressure favoured the nitro isomer. The difference in molecular volumes were found [172] to be -7.2 ± 1 cm^3 mol^{-1} and -4.5 ± 0.8 cm^3 mol^{-1} for Ni(*NN'*-dieen)$_2$(NO$_2$)$_2$ and Ni(*NN*-dimen)$_2$(NO$_2$)$_2$, respectively. It was noted [172] that these values are in poor agreement with the results of density measurements made on the two isomeric forms of Ni(*NN'*-dieen)$_2$(NO$_2$)$_2$ isolated in the solid state ($\Delta V \approx -30$ cm^3 mol^{-1}) [171]. However, this is not surprising, since the stable form of solid Ni(*NN'*-dieen)$_2$(NO$_2$)$_2$ does not in fact consist of molecules involving monodentate nitrito groups. Instead, the solid is composed of [Ni(*NN'*-dieen)$_2$(*O*$_2$N)]$^+$ units containing chelating nitrite ions, the second nitrite being present as an uncoordinated counter-ion [31]. Since a solution of the complex in chloroform is non-conducting [88], it would seem that this compound exists in three forms, changing from the species containing chelating nitrite ions in the solid state to a mixture of molecules containing monodentate nitro and nitrito groups upon solution in an inert solvent. The preparation of an unstable solid pink form of the complex has been reported [170,171], and it was suggested that this is probably the nitro isomer of the compound.

In each of the above studies it was assumed that the equilibrium is between a dinitro and a dinitrito complex. This was because it was considered that a mixed nitro-nitrito complex of the form Ni(diamine)(*O*NO)(*N*O$_2$) would probably have an electronic spectrum intermediate between those observed for typical dinitrito and dinitro complexes, i.e., a peak at ~ 18500 cm^{-1}, intermediate between those at ~ 17000 and ~ 20000 cm^{-1} observed for dinitrito and dinitro complexes, respectively [88]. However, recent work has shown that this is not expected to be the case [see section E(ii)(d)], since the peak at ~ 20000 cm^{-1} characteristic of nickel(II) bonded to nitrite via nitrogen is not "*d–d*" in origin. In fact, a mixed nitro-nitrito complex would probably have a spectrum similar to that observed [116] for the nitro-aquo complex [Ni(*NN*-dimen)$_2$(*N*O$_2$)(H$_2$O)]ClO$_4$, which shows bands centred at ~ 17500 and ~ 20500 cm^{-1} (Fig. 14). Thus, while it is quite feasible that the above equilibria involve just dinitro and dinitrito species, the possibility that a mixed nitro-nitrito complex is involved cannot be excluded on the evidence presently available.

It has been reported by Green [171] that when the red nitro complex Ni(en)$_2$(NO$_2$)$_2$ is heated to 120°C it changes to a blue form, and it was concluded that this is probably the nitrito isomer of this molecule. However, the IR spectrum of the blue species showed a strong nitrite peak at ~ 1205 cm^{-1}, and this is characteristic of a chelating anion, rather than a monodentate oxygen-bonded nitrite [see section E(i)(c)]. It thus seems more likely that on heating, the nitro complex Ni(en)$_2$(*N*O$_2$)$_2$ undergoes a change to an isomeric form $[Ni(en)_2(O_2N)]NO_2$ containing one chelating and one non-bonded ionic nitrite. The ionic species would also contribute to the IR absorption at 1205 cm^{-1}. It is to be noted that both the analogous zinc complex, $Zn(en)_2(NO_2)_2$ [27], and several complexes of the type $Ni(diamine)_2(NO_2)_2$ [30,31], where diamine represents a substituted ethylenediamine are known to contain one chelated and one non-bonded nitrite group. The pressure dependence of the equilibrium between the blue and red forms of $Ni(en)_2(NO_2)_2$ has been studied by Ferraro and Fabrizzi using IR spectroscopy [173]. The results were interpreted in terms of a shift from the nitrito to the nitro form upon an increase in pressure, but in view of the above conclusions it seems more likely that the change is from chelation to nitro coordination of the nitrite groups.

The IR spectrum of the solid complex $Ni(i\text{-}quin)_4(NO_2)_2$ is unusual, since it shows peaks characteristic of the presence of both monodentate nitro and nitrito groups [25]. Moreover, the electronic spectrum of this compound shows peaks at both 17000 and 20500 cm^{-1}, looking quite similar to the solution spectra above. On the basis of this spectral evidence, Goodgame and Hitchman [25] suggested that the solid complex probably consists of a mixture of linkage isomers of the type $Ni(i\text{-}quin)_4(ONO)_2$ and $Ni(i\text{-}quin)_4(NO_2)_2$. The possibility that a mixed nitro-nitrito species of the type $Ni(i\text{-}quin)_4(ONO)(NO_2)$ might be present was considered unlikely, since it was thought this would have a peak in the electronic spectrum intermediate between those shown by analogous nitrito and nitro complexes. However, this is now known to be incorrect (see arguments above), and it seems quite likely that a mixed nitro-nitrito molecule would have an electronic spectrum quite similar to that observed for solid $Ni(i\text{-}quin)_4(NO_2)_2$. The effect of pressure on the IR spectrum of the complex has been investigated recently by Hitchman and Ahsbahs [174], who observed that on raising the pressure the peaks assigned to nitrito groups progressively decreased in intensity, while those assigned to the nitro groups showed a corresponding increase. The changes occurred continuously and reversibly, with the complex being converted essentially completely to the nitro form by ~20 kbar. These results confirm the presence of both nitro and nitrito groups in the compound, with the nitro isomeric form having the smaller molecular volume. The X-ray powder diffraction pattern of the complex did not alter noticeably during the change and this fact, together with the continuous and reversible nature of the conversion, was taken to suggest that the compound may well be of the form $Ni(i\text{-}quin)_4(NO_2)_x(ONO)_{2-x}$, in which the electronic and steric forces which decide the manner of nitrite coordination are delicately balanced, giving rise to a statistical distribution of nitro and nitrito groups bound to the nickel(II) ion. It is interesting to note that in $Co(i\text{-}quin)_4(NO_2)_2$ [23] and in complexes of the form $Ni(L)_4(NO_2)_2$ [25,28], where L is an aromatic amine such as pyridine, the nitrite groups are in every case coordinated via oxygen. It has been inferred that this form of bonding occurs because it minimizes steric interaction between the nitrite and amine ligands, and it is perhaps surprising that in the isoquinoline complex of nickel a lesser degree of interligand steric crowding apparently prevails than in other molecules of this kind. However, it should be noted that these interactions are expected to be very dependent on the "pitch" of the amine rings in this type of complex, the angle between the plane of the amine and the plane orthogonal to the nickel–nitrite bond directions being typically ~ 55° [28]. It has been suggested [25] that intermolecular packing considerations may produce a comparatively low value of this angle in the isoquinoline complex, hence reducing the steric crowding within each molecule. It is unfortunate that so far it has not proved possible to prepare single crystals of $Ni(i\text{-}quin)_4(NO_2)_2$ of good enough quality to allow an X-ray diffraction study so that this hypothesis may be tested.

Another example of what may loosely be termed linkage isomerism concerns the compound originally formulated as $K_4Ni(NO_2)_6$ [78,86,175]. An early crystal structure of this compound [175] reported that it contained a regular, octahedral hexanitro nickel(II) ion. Goodgame and Hitchman [7] noticed that on heating to 120°C the compound changed from an orange to a brick-red colour, the original colour returning on cooling in the atmosphere. Subsequent investigation showed that the orange complex is in fact a monohydrate, and that the removal of the water molecule by heating produces a red product which is quite stable under anhydrous conditions. This observation has been confirmed by Brooker and Irish [107]. It was suggested [7] on the basis of the IR and electronic spectra that the red product contains some nitrite groups bound via nitrogen, and some via oxygen. The IR frequencies, and the close similarity of the spectra to those of the $Ni(NO_2)_5^{3-}$ ions present in $M_3Ni(NO_2)_5$, $M = Rb$ and Cs [7], suggest that the red form of $K_4Ni(NO_2)_6$ probably contains both nitro groups and chelating nitrite ions, and may well be of the form $K_4[Ni(\mathit{N}O_2)_4(\mathit{O}_2N)]NO_2^-$.

H. THE NATURE OF THE METAL–NITRITE BOND

Since it is well established that the way in which the nitrite ion functions as a ligand depends upon the nature of the metal to which it is bonded, and that the electronic spectral characteristics of the complex depend upon the type of nitrite coordination, it is pertinent to ask whether these factors can be rationalized in terms of effects such as the capacity of the nitrite to undergo σ- and π-bond formation with the metal. A simple picture of the bonding in the nitrite ion itself considers that the oxygen atoms are bound to the nitrogen via sp^2 hybrid orbitals, leaving two lone pairs of electrons on

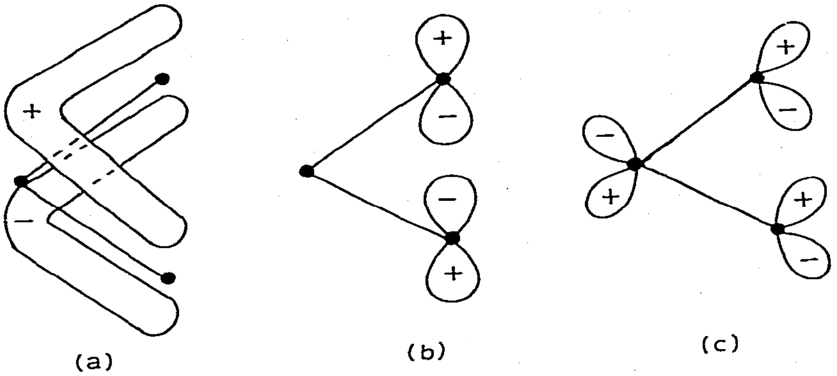


Fig. 20. The bonding (a), non-bonding (b) and antibonding (c) π-molecular orbitals of the nitrite ion.

each oxygen, and one lone pair on the nitrogen. Each orbital containing a lone pair has the potential to form a σ-bond to a metal ion. The remaining p orbitals are orthogonal to the plane of the ion, and overlap to form the three π-molecular orbitals illustrated in Fig. 20, with the bonding and non-bonding orbitals being filled with electrons.

The two most striking differences observed experimentally between the nitrite ion acting as a ligand via nitrogen or oxygen are the relative position of these groups in the spectrochemical series, and the way in which the manner of coordination depends upon the nature of the metal ion. Considering the first of these points, when bound via oxygen the nitrite is a relatively weak ligand, while when bonded via nitrogen it is rather strong. This behaviour is seemingly independent of the nature and oxidation state of the metal, being similar for nickel(II), cobalt(II) and cobalt(III). Typical values of the ligand-field splitting parameters appropriate to six ligands in an octahedral nickel(II) complex are $\Delta_0(NO_2) \approx 13000$ cm^{-1}, and $\Delta_0(ONO) = 7000–9000$ cm^{-1} the range of values observed for the monodentate nitrito group apparently depending on the metal–oxygen bond distance in the complex [see section E(ii)(d)]. These may be compared with the value $\Delta_0 \approx 11500$ cm^{-1} for the Ni(en)$_3^{2+}$ ion [176]. The parameter Δ_0 is expected to depend upon both the σ- and π-bonding interactions of the ligand with the metal, and in general weak ligands are expected to be π-donors and "strong" ligands π-acceptors, compared with ligands such as ethylenediamine which cannot participate in π-bond formation. The little quantitative data which are available seems to be in agreement with these suggestions, with ligands such as H_2O, Cl^-, Br^- and F^- being σ- and π-donors towards metal ions such as Ni(II), Cu(II), Co(III) and Cr(III), while pyridine acts as either a very weak π-donor, or π-acceptor to Ni(II) and Cr(III) [177], and phosphines are found to act as σ-donors and π-acceptors towards Co(II) [178]. The most direct evidence of the relative σ- and π-bonding effects in metal–ligand bonds is probably provided by an analysis of the band splittings observed in the electronic spectrum of low-symmetry complexes. The application of this kind of analysis to nitrite complexes is complicated by the fact that the π-bonding parameters are expected to be highly anisotropic with respect to the metal–ligand bond axis, being close to zero in the plane of the ion (Fig. 20), a fact which has often been ignored in the analysis of the electronic spectra of nitrite complexes [28,29,132,133]. So far, the only detailed studies of electronic spectra to provide information on the nature of the metal–nitrite bond have been carried out on nickel(II) complexes. Walker et al. [179] have analysed the polarized spectra of several complexes of the type $[\mathrm{Ni(diamine)_2}(O_2\mathrm{N})_2]\mathrm{NO_2}$ and $\mathrm{Ni(diamine)}(O_2\mathrm{N})_2$ containing chelating nitrito groups. Making the reasonable assumption that the in-plane π-interaction from the nitrite is negligible, these workers derived the angular overlap parameters $e_\sigma \simeq 2500$ cm^{-1}, $e_\pi \simeq 500$ cm^{-1} for a chelating nitrito oxygen atom towards nickel(II). This corresponds to a value $\Delta_0 \simeq 6500$ cm^{-1}, in good agreement with the values observed for weakly bound monodentate nitrito groups towards this metal ion [29]. The band splittings observed in the electronic spectrum of the complex $\mathrm{Ni(pyr)_4}(O\mathrm{NO})_2$ have been analysed by Finney et al. [28], and assuming that the π-bonding parameters of both the pyrazole and nitrite ligands are isotropic about the metal–ligand bond axis, and that the pyrazole ligands have similar bonding parameters, to those in the analogous chloro complex [180], values of $e_\sigma \simeq 3000$ cm^{-1}, $e_\pi \simeq 100$ cm^{-1} were derived for the monodentate nitrito group towards nickel(II). Considering the approximations involved, these figures should only be taken as giving a qualitative guide to the bonding properties of the nitrite. However, remembering that the parameters represent the energy by which a *d* orbital is raised upon interaction with one ligand, they do suggest that when bound via oxygen the nitrite is a considerably weaker σ-donor than, say, ethylenediamine ($e_\sigma \simeq 3750$ cm^{-1}) and also acts as a weak π-donor.

The single-crystal polarized spectra of the *trans* nitro complexes $\mathrm{Ni(NH_3)_4}(N\mathrm{O_2})_2$ [132] and $\mathrm{Ni(en)_2}(N\mathrm{O_2})_2$ [133] have also been reported and analysed in terms of the ligand-field splitting parameters of the nitro group. The parameters suggest that the nitro group is a slightly stronger σ-donor than the amine ligands, and also acts as a π-acceptor. However, in order to derive the bonding parameters it was assumed that the second band in the spectrum of each complex is a "*d–d*" transition, and subsequent work has shown that this is not the case [see section E(ii)(d)]. As it is impossible to derive independent values for the σ- and π-bonding parameters from the splitting of just the first ligand-field band of a nickel(II) complex, this information unfortunately cannot be obtained from an analysis of the spectra of a *trans* nickel nitro complex. The electronic spectrum of the tetragonally elongated $\mathrm{Cu}(N\mathrm{O}_2)_6^{4-}$ ion has been reported by several groups of workers [77,124,140]. From the energy of the transition $^2B_{1g}(d_{x^2-y^2}) \leftarrow {}^2A_{1g}(d_{z^2})$ Reinen and Friebel have deduced a value of $e_\sigma \approx 4000\ \mathrm{cm}^{-1}$ for the nitro group towards copper(II) in a hypothetical regular octahedral complex [124], a value similar to that obtained for ethylenediamine towards this metal ion. Since no discernible splitting of the transitions $^2E_g(d_{xz}, d_{yz})$, $^2B_{2g}(d_{xy}) \leftarrow {}^2B_{1g}(d_{x^2-y^2})$ is observed for the $\mathrm{Cu}(N\mathrm{O}_2)_6^{4-}$ species. Reinen has concluded that the π-bonding effect of the nitro groups in this complex is small [124,142]. Molecular-orbital calculations suggest [181] that a weak π-antibonding effect may be present, while an analysis [182] of the g anisotropy in $\mathrm{K}_2\mathrm{BaCu}(N\mathrm{O}_2)_6$ implies that the nitro groups may act as weak π-acceptors.

Although the evidence is at present patchy, the general picture to emerge from an analysis of the electronic spectra of nitrite complexes is that when this ligand bonds via oxygen it produces a much weaker σ-interaction than when it binds via nitrogen. Also, when bonded via oxygen, it acts as a weak π-donor, while when coordinated via nitrogen the π-interaction is probably quite small, the sign of the interaction in this case being uncertain. What is clear, is that the combined effect of the σ- and π-bonding interaction is such that the overall d-orbital splitting is ~75% greater for an octahedral nitro complex compared with the value produced by six oxygen-bound nitrite groups. This view of the bonding characteristics of the nitro group is confirmed by the analysis of the Mössbauer spectrum of the $\mathrm{Fe}(N\mathrm{O}_2)_6^{4-}$ ion, which has been interpreted as indicating that when bound in this manner, the nitrite forms strong σ-bonds with the metal, and participates in weak π-bond formation [156]. Similarly, the strong *trans* directing effect of the nitro group in the reaction kinetics of Pt(II) complexes has been discussed in terms of this ligand probably acting as a π-acceptor ligand [183].

It is of interest to see whether the dependence of the metal–ligand interaction upon the type of atom coordinated to the metal can be correlated with the electronic structure of the nitrite ion. The fact that the nitrite functions as a stronger σ-donor when bonded via nitrogen compared with oxygen is in agreement with the fact that transition metal complexes involving simple nitrogen ligands are generally more covalent and more stable than those involving oxygen donors. As far as the π-interactions are concerned, it is noteworthy that the highest-filled orbital of π-symmetry, the non-bonding orbital [Fig. 20(b)], is localized largely on the two oxygen atoms. This is consistent with the fact that the nitrite functions as a π-donor when bonded via oxygen. The lobes of the empty π^* orbital are directed in such a manner that they will overlap effectively with metal t_{2g} orbitals when the nitrite bonds via nitrogen, but not when it bonds via oxygen. This suggests that the nitrite ion can only function as a π-acceptor when it bonds via nitrogen, which is also in agreement with the above conclusions. Indeed, a simplistic picture of the interaction of the nitro group with a metal would suggest that this could act as a π-donor or a π-acceptor depending on whether the bonding or antibonding nitrite π-orbitals are closer in energy to the metal t_{2g} orbitals.

It is also pertinent to consider whether these ideas concerning the nature of the metal–nitrite bond are consistent with the relative stabilities observed for the different modes of coordination to various metal ions. Considering just those metals for which a significant amount of data are available, nitrite coordination to chromium(III) and zinc(II) takes place exclusively via oxygen, while for thermodynamically stable complexes of Co(III), Rh(III), Ir(III), Pt(II) and Pt(IV) the nitrite invariably bonds via nitrogen. The metal ions Cd(II), Co(II), Ni(II) and Cu(II) all form some complexes involving nitrogen-bound nitrite groups, and others in which the nitrite is coordinated via oxygen. These differences are consistent with the concept that on complex formation the metal ions Cr(III) and Zn(II) function as "hard" Lewis acids, while Pt(II), Co(III), Rh(III), Ir(III) and Pt(IV) act as "soft" acids, with the divalent ions Cd(II), Co(II), Ni(II) and Cu(II) lying between these extremes. The trends in nitrite coordination are then explained by assuming that this ligand functions as a "hard" base when it bonds via oxygen, but a "soft" base when coordinated via nitrogen. Similar arguments have been used to rationalize the fact that the thiocyanate ligand tends to bond via nitrogen to first-row transition ions, but via sulphur to heavier elements [184]. At a more quantitative level, the marked distinction between the behaviour of chromium(III) on the one hand, and cobalt(III) and platinum(II) on the other may well be due to the different capabilities of these metal ions to participate in π-bond formation with the nitrite. The chromium(III) ion has a half-filled set of t_{2g} orbitals, so that interaction with filled ligand orbitals of π-symmetry produces a net bonding interaction. For the low-spin d^6 and d^8 electron configurations of cobalt(III) and platinum(II), however, the t_{2g} orbitals are full, so that a π-interaction may only help to stabilize the formation of a complex when this occurs with empty ligand orbitals. Arguments of this kind have been used to explain the fact that very strong bonds are apparently formed between Cr(III) and π-donors such as F^- and OH^-, while the corresponding bonds formed by Co(III) are much weaker [185]. The fact that the nitrite acts as a π-donor when bonded via oxygen, but may act as a π-acceptor when bound via nitrogen could therefore be an important factor in making the former mode of coordination more stable for chromium(III), while the latter is preferred for cobalt(III) and platinum(II). The propensity of zinc(II) to coordinate to the nitrite ion solely via oxygen cannot be explained by similar arguments. Possibly, in this case, the tendency is simply a reflection of the greater ionic character associated with the bonding to this metal ion, as compared with the later metals of the transition series.

I. GENERAL CONCLUSIONS

Much of the interest in transition metal nitrite complexes derives from the fact that this ligand can bind to a metal in a variety of different ways, and the manner of bonding is clearly influenced both by the electronic structure of the metal ion, and by the extent of interligand repulsions within a complex. Each type of nitrite coordination gives rise to particular spectroscopic characteristics, and these provide a means not only of identifying the mode of bonding present in a complex, but also of investigating the nature of the metal–ligand interaction. While a wide range of physical techniques has been applied to the study of nitrite complexes, certain areas have not as yet been fully exploited. In particular, it seems likely that a comprehensive study of the way in which the Raman, and nitrogen and oxygen NMR spectral frequencies of the nitrite group vary as a function of its manner of coordination would be worthwhile.

It is also apparent that the majority of nitrite complexes prepared so far involve a relatively small number of metal ions, with the compounds formed by chromium, cobalt, nickel, copper, zinc, and platinum having received the most attention. In order that a more balanced view should be obtained, it is clearly desirable that future experimental work should be directed towards the preparation of complexes of the middle and earlier first-row transition elements, as well as members of the second and third transition series. When combined with previous work, this should provide a much more complete picture of the chemistry and bonding characteristics of that versatile ligand, the nitrite ion.

APPENDIX

Metal–ligand bond lengths and nitrite geometry in complexes studied by single crystal X-ray and neutron diffraction

Ligand abbreviations

3,2,3-TET	1,10-diamino-4,7-diazadecane
1,9-DiMAD	1,9-dimethyladeninium
acac	acetylacetonato
DEOXYAD	deoxyadenosine
TRIC	tricanthine
DMF	dimethylformamide

2-AMPYM	2-aminopyrimidine
DIEN	diethylenetriamine
1,3-DAP	1,3-diaminopropane
1,9-DIAMDITH	1,9-diamino-3,7-dithiononane
1,4,7,10-TETAZ	1,4,7,10-tetra-azacyclododecane
23′2	5-methyl-1,4,8,11-tetra-azaundecane
en	ethane-1,2-diamine
(N^2-Me-(*S*)-pn)	(2*s*)-2-amino-4-azapentane
1,2-PROPEN	(−) 589-1,2 propylenediamine
L-3,8-dimetrien	L-3,8-dimethyltriethylenetetramine
MAL	malonate
enacet	ethylenediaminetriacetate
GLYO	glycinate
β-ALAN	β-alaninate
DIDIDOD	2*R*,11*R*-diamino-4*R*,9*R*-dimethyl-5,8-diazadodecane
l-ARG	l-arginine
oxo	oxalate
l-histo	l-histidinate
R-5 metrien	*R*-5-methyltriethylenetetramine
3,5-lut	3,5-lutidine
TPP	αβγδ-tetraphenylporphinate
1,2,3-TAP	1,2,3-triaminopropane
trien	trimethylenediamine
NN′-dimen	*NN′*-dimethylethane-1,2-diamine
NN-dimen	*NN*-dimethylethane-1,2-diamine
N-PPD	*N*-isopropyl-2-methyl-1,2-propanediamine
2,2′-Bipy	2,2′-bipyridyl
Et$_4$dien	tetraethyldiethylenetriamine
DIM-1,10-PHEN	2,9-dimethyl-1,10 phenanthroline
ent	ethylenetriamine
py	pyridine
2-meim	2-methylimidazole
4-mepy	4-methylpyridine
NNN′N′-tetmen	*NNN′N′*-tetramethylethane-1,2-diamine
NN′-dieen	*NN′*-diethylethane-1,2-diamine
NN-dieen	*NN*-diethylethane-1,2-diamine
DMG	dimethylglyoxime
DMGH$_2$	dimethylglyoximate
Me$_6$[14]4,11-dieneN$_4$	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
sal$_2$en	*N*,*N′*-ethylenebis(salicylaldiminato)
PnAO-H	2,2′-1,3-diaminopropanebis(2-methyl-3-butanone)

Complex	Bond lengths (Å)			∠ONO (°)	R factor	Comments	Ref.
	M–L	N–O					
Monodentate nitro groups bonded to Co(III) and Co(II)							
(+) t[Co(3,2,3-TET)$(NO_2)_2$Br	1.943(7)	1.242(9)	1.210(11)	119.1(7)	0.038	a,b	191
	1.946(7)	1.223(9)	1.215(12)	119.0(8)			
[Co(1,9-DiMAD)$(acac)_2(NO_2)]^+$	1.911(6)	1.22(1)	1.21(1)	120.9(6)			
$[Co(acac)_2(NO_2)_2]^-$	1.950(7)	1.24(1)	1.20(1)	117.2(7)	0.086	b	192
	1.926(6)	1.23(1)	1.25(1)	116.6(6)			
t-$[Co(NH_3)_4(NO_2)_2]CH_3COO$	1.932(3)	1.240(4)		120.9(2)	0.044	a,b	193
	1.941(3)	1.244(4)		118.6(2)			
[Co(DEOXYAD)$(acac)_2(NO_2)]\cdot 3\cdot 5H_2O$	1.90(3)	1.22(4)	1.23(6)	118(2)	0.116	c	194
[Co(TRIC)$(acac)_2(NO_2)]\cdot H_2O\cdot$DMF	1.915(4)	1.218(5)	1.216(5)	120.1(4)	0.064	a,b	195
[Co(2-AMPYM)$(acac)_2(NO_2)$]	1.900(10)	–		–	0.102	d,e	196
t[Co(py)$(NO_2)(NH_3)_4]Br_2\cdot H_2O$	1.892(13)	1.235(17)	1.245(17)	118.5(14)	0.059	–	197
[Co(DIEN)$(NO_2)(H_2O)(NH_3)](ClO_4)_2\cdot H_2O$	–			–		d	198
[Co(PnAO-H)$(NO_2)_2$]	1.984(3)	1.250(3)	1.232(3)	118.4(2)	0.035	a,b	199
[Co(1,9-DIAMDITH)(NO_2)Cl]Cl	2.09(1)	1.12(1)	1.13(1)	130.8(2)	0.060	b	200
[Co(1,4,7,10-TETAZ)$(NO_2)_2]Cl\cdot H_2O$	1.923(5)	1.239(7)	1.240(7)	119.3(6)	0.026	a,b	201
	1.931(5)	1.221(6)	1.223(6)	120.8(5)			
[Co(β-ALAN)(1,3-DAP)$(NO_2)_2]\cdot H_2O$	–	–		–	0.056	d	202
$\beta(+)$*cis*-[Co(23′2)$(NO_2)_2$]Br	1.932(4)	1.225(5)	1.236(5)	119.6(4)	0.034	a,b	203
	1.929(3)	1.216(6)	1.239(5)	120.0(3)			
t-$[Co(en)_2(NO_2)_2](NO_3)$	1.939(2)	1.228(4)	1.224(4)	119.8(2)	0.050	a,b	204
	1.937(2)	1.238(4)	1.236(4)	120.6(2)			
mer-$[Co(NH_3)(en)(NO_2)_3]$ Yellow	1.936(7)	1.226(10)	1.224(10)	119.9(7)	0.066	a,b	205
	1.926(8)	1.226(11)	1.241(10)	120.6(7)			
	1.929(8)	1.232(10)	1.250(10)	120.2(7)			
mer-$[Co(NH_3)(en)(NO_2)_3]$ Brown	1.938(7)	1.194(8)	1.207(9)	117.0(9)	0.058	a,b	
	1.924(6)	1.217(7)	1.206(8)	117.8(6)			
	1.944(6)	1.226(8)	1.224(6)	117.0(5)			
Co(dien)$(NO_2)_3$	–	–		–	–	d	206

Complex	Bond lengths (Å)			∠ONO (°)	R factor	Comments	Ref.
	M–L	N–O					
$[Co(dien)(NH_3)(NO_2)_2](BF_4)$	–	–		–		d	207
$[Co(N^2\text{-}Me(S)\text{-}pn)(NO_2)_2]Cl$	1.946(6)	1.204(11)	1.171(12)	118.4(8)	0.039	a,b	208
	1.936(6)	1.229(9)	1.239(9)	118.8(6)			
(+)*cis*-$[Co(1,2\text{-}PROPEN)_2(NO_2)_2]Cl$	1.88(2)	1.22(3)	1.24(3)	117(2)	0.12	–	209
	1.92(3)	1.27(3)	1.20(3)	118(3)			
t$[Co(L\text{-}3,8\text{-}dimetrien)(NO_2)_2]ClO_4$	1.93(2)	1.19(3)	1.22(3)	116.6(18)	0.088	–	210
	1.98(2)	1.17(3)	1.26(3)	119.7(20)			
$[Co(en)(NH_3)_2(NO_2)_2]NO_3$	–	–		–		d	211
$[Co(en)_2(NO_2)_2]^+$	1.93(2)	1.20(3)	1.26(3)	121(2)	0.101	–	212
$[Co(en)(MAL)_2]^-$	1.95(2)	1.18(3)	1.25(3)	119(2)	0.101	–	212
$[Co(en)_2(NCS)(NO_2)]NCS$	1.914(7)	1.210(11)	1.189(11)	–	0.077	a,b	213
t$[Co(en)_2(NO_2)(NCS)]I$	1.897(10)	1.23(2)	1.23(1)	120.2(11)	0.049		
t$[Co(en)_2(NO_2)(NCS)]ClO_4$	1.881(18)	1.22(3)	1.22(2)	121.5(20)	0.103	a,b	214
$[Co(TPP)(DMGH_2)_2(NO_2)]$	1.980(10)	1.21(2)	1.25(2)	119(1)	0.049	–	215
$Na[Co(DMGH_2)(DMG)(NO_2)_2]\cdot 2H_2O$	1.943(3)	1.250(4)	1.230(4)	120.0(3)	0.049	a,b	
$[Co(en)(NH_3)(NO_2)_2(NCS)]$	–	–		–		d	216
$K[Co(enacet)(NO_2)]\cdot 1.5H_2O$	1.923(3)	1.231(3)	1.231(3)	119.6(3)	0.045	a,b	217
$K[Co(GLYO)(NO_2)_3]$	–	–		–		d	218
t$[Co(1,3\text{-}DAP)(\beta\text{-}ALAN)(NO_2)_2]$	1.912(6)	1.235(7)	1.231(7)	117.7(7)	0.057	a,b	219
	1.980(6)	1.229(8)	1.234(8)	119.5(6)			
$K[Co(\beta\ ALAN)_2(NO_2)_2]$	1.941(11)	1.268(14)	1.241(14)	119.2(11)	0.118	–	220
(+)$[Co(l\text{-}ALAN)(NH_3)_2(NO_2)_2]$	–	–		–	–	d	221
t$[Co(DIDIDOD)(NO_2)_2]NO_2$	–	–		–	0.049	d	222
rac-c$[Co(1,3\text{-}DAP)_2(NO_2)_3]Cl\cdot H_2O$	1.924(3)	1.237(3)	1.234(3)	119.1(3)	0.027	a,b	223
	1.936(3)	1.232(4)	1.232(4)	120.0(3)			
(+)$[Co(l\text{-}ARG)_2(NO_2)_2]NO_3\cdot 2H_2O$	1.894(7)	1.240(9)	1.201(9)	120.1(7)	0.075	a,b	224
	1.941(7)	1.205(11)	1.194(12)	124.0(7)			
$Ag[(+)c\text{-}Co(D\text{-}ALAN)_2(NO_2)_2]$	1.87(2)	1.22(3)	1.23(4)	118(2)	0.085	–	225
$[Co(GLYO)_2(NH_3)_2(NO_2)]\cdot H_2O$	1.875(7)	1.226(9)	1.225(9)	119.8(7)	0.068	a,b	226
c$[Co(en)_2(NO_2)_2]^+$ $[Co(en)(NO_2)_4]^-\cdot H_2O$	–	–		–	0.13	d	227

$[Co(en)_2(NO_2)_2]^+$	1.925(5)	1.213(10)	1.165(10)	116.6(7)			
	1.929(5)	1.172(10)	1.216(8)	116.0(6)			
$[Co(NH_3)_2(oxo)(NO_2)_2]^- \cdot H_2O$	1.911(7)	1.189(11)	1.155(13)	115.4(9)	0.041	a,b	228
	1.890(6)	1.169(10)	1.145(14)	113.0(9)			
$K[Co(GLYO)(NH_3)(NO_2)_3] \cdot H_2O$	1.920(7)	1.225(8)	1.258(8)	117.9(7)	0.048	a,b	229
	1.929(7)	1.218(8)	1.233(8)	118.5(7)			
t[Co(l-histo)$_2$(NO$_2$)$_2$]$\cdot$H$_2$O	–			–	0.076	d	230
$c[Co(en)_2(NO_2)_2]NO_3$	1.887(17)	1.229(22)	1.231(22)	116.1(19)	–	–	204
	1.918(18)	1.211(26)	1.226(26)	118.7(18)			
cis-β[Co(*R*-5 metrien)(NO$_2$)$_2$]Cl	1.922(10)	1.220(13)	1.237(13)	117.7(9)	0.069	–	231
	1.938(10)	1.205(15)	1.205(14)	119.1(8)			
cis-β[Co(L-3,8-dimetrien)(NO$_2$)$_2$]ClO$_4$	1.941(17)	1.223(22)	1.241(22)	119.2(16)	0.093	–	232
	1.923(16)	1.217(21)	1.244(21)	117.6(15)			
[Co(3,5-lut)(TPP)(NO$_2$)]	1.948(4)	1.155(5)		115.4(6)	0.045	a,b	233
[Co(1,2,3-TAP)(NO$_2$)$_3$]	–	–		–	–	d	234
$[Co(NH_3)_5(NO_2)]Cl_2$	–	–		–	–	d	235
$K_2BaCo(NO_2)_6$	1.93(6)	1.25(4)		113(5)			
	2.10(2)	1.31(3)		118(3)	0.09	c	130, 236
	1.91(2)	1.26(2)		115(2)			
$Co(NH_3)_3(NO_2)_3$	1.93(1)	1.22(2)	1.22(2)	119(2)			
	1.90(1)	1.26(2)	1.25(2)	114(2)	0.090	–	237
	1.92(1)	1.26(2)	1.22(2)	118(2)			
$[Co(trien)_2(NO_2)_2]NO_2$	1.926(6)	1.237(7)	1.235(8)	119.1(4)	0.062	a,b	238
$Co(NH_3)_5(NO_2)]Br_2$	1.921(21)	1.161(22)	113.9(19)		0.080	–	239
c-α[Co(L-3,8-dimetrien)(NO$_2$)$_2$]ClO$_4$	–	–		–	0.09	d	232
$[Co(en)_2(NO_2)]_2O_2(NO_3)_2 \cdot 4H_2O$	1.940(8)	1.204(14)	1.238(13)	117.1(10)	0.106	–	240
Monodentate nitro groups bonded to nickel(II)							
$Ni(NH_3)_4(NO_2)_2$ 130 K	2.141(2)	1.250(2)	1.264(2)	117.3(2)	0.028		
$Ni(NH_3)_4(NO_2)_2$ 295 K	2.150(2)	1.240(3)	1.255(4)	117.0(3)	0.051	a,b	241
$Ni(en)_2(NO_2)_2$	2.130(3)	1.243(4)	1.234(3)	117.0(3)	0.044	a,b	14
[Ni(*NN*′-dimen)$_2$(NO$_2$)$_2$]$\cdot$H$_2$O	2.129(3)	1.236(4)	1.243(4)	116.8(2)	0.040	a,b	14
	2.113(3)	1.225(4)	1.228(5)	116.8(3)			
[Ni(*NN*-dimen)$_2$(NO$_2$)(H$_2$O)]ClO$_4$	2.122(4)	1.221(5)	1.244(5)	116.2(4)	0.050	a,b	116
$K_2Ba[Ni(NO_2)_6]$	2.080(2)	1.248(2)		117.2(2)	0.017	a,b	242
$K_2Sr[Ni(NO_2)_6]$	2.078(1)	1.248(2)		116.4(1)	0.026	a,b	138
$K_2Pb[Ni(NO_2)_6]$	2.080(2)	1.245(2)		117.3(2)	0.016	a,b	249

Complex	Bond lengths (Å)			∠ONO (°)	*R* factor	Comments	Ref.
	M–L	N–O					
$Ni(en)_2(NO_2)_2 \cdot H_2O$	2.09(1)	–		–	0.125	d	9
$Ni(en)_2(NO_2)(NCS)$	–	–		–	–	d	243
Monodentate nitro groups bonded to copper(II)							
$Cu(1,3\text{-}DAP)_2(NO_2)_2$	2.655(8)	1.243(10)	1.170(12)	114.8(8)	0.076	–	244
$[Cu(N\text{-}PPD)_2(NO_2)]NO_2$	2.052(20)	1.11(5)	1.08(4)		0.051	c	245
$Cu(NH_3)_4(NO_2)_2$	2.65(3)	1.23(3)		117(4)	–	d,e	246
$K_3[Cu(NO_2)_5]$	f	f		f	0.056	f	34
$K_2Ca[Cu(NO_2)_6]$	2.050(1) 2.052(1) 2.313(1)	1.246(1) 1.246(1) 1.252(1)		116.6(1) 116.7(1) 115.2(1)	0.032	a,b	138
$K_2Sr[Cu(NO_2)_6]$	2.029(2) 2.041(2) 2.310(2)	1.246(1) 1.242(1) 1.251(1)		116.7(1) 117.1(1) 115.8(1)	0.031	a,b	138
$K_2Ba[Cu(NO_2)_6]$	2.038(2) 2.048(2) 2.311(2)	1.232(2) 1.229(2) 1.236(2)		117.6(2) 117.3(2) 116.0(2)	0.016	a,b	138
$K_2Pb[Cu(NO_2)_6]$	2.111(4)	1.260(4)		117.9(4)	0.028	a,b	247
$Rb_2Pb[Cu(NO_2)_6]$	2.063(3) 2.173(4) 2.173(4)	1.243(2) 1.240(3) 1.248(3)		117.4(3) 116.0(4) 115.5(4)	0.026	a,b	139
$Tl_2Pb[Cu(NO_2)_6]$	2.118(6)	1.252(4)		116.6(5)	0.036	a,b	139
Monodentate nitro groups bonded to other metal ions							
$\mu oxo[Ru(bipy)_2(NO_2)](ClO_4)_2 \cdot 2H_2O$	2.067(11) 2.034(8)	1.242(9) 1.224(9)	1.243(9) 1.264(9)	118.2(8) 116.2(7)	0.06	a	248
$Na_2[Ru(NO_2)_4(NO)(OH)] \cdot 2H_2O$	2.080(3) 2.078(3)	1.212(5) 1.213(5)	1.211(4) 1.207(5)	120.1(4) 118.3(4)	0.098	a	250
$[Pd(NO_2)(NH_3)_3]_2[Pd(NH_3)_4](NO_3)_4$	1.984(8)	1.104(7)		115.2(9)	0.037	a	91
$[Pd(dien)(NO_2)]NO_3$	2.028(7)	1.241(7)	1.208(7)	118.5	0.034	a	251
$Pd(Et_4dien)(NO_2)]NO_3 \cdot H_2O$	2.05(2)	1.16(3)	1.23(3)	121	0.052	–	251

Pd(DIM-1,10-PHEN)$(NO_2)_2$	–	–		–	–	d	252
Pt(en)$Cl_2(NO_2)_2$	2.137(3) 2.003(2)	1.22(3) 1.15(3)	1.26(3) 1.35(4)	127(3) 118(2)	0.063	–	253
K[Pt(GLYO)$(NO_2)_2$]·H_2O	–	–		–	–	d	254
[Pt(ent)(NO_2)]I	–	–		–	–	d	255
t[Pt(P(p-$C_6H_4CH_3)_3)_2(NO_2)_2$]	2.030(5)	1.228(8)	1.198(7)	121.7(6)	0.043	a	256
[Cr(Me_6[14]4,11-dieneN_4)(NO_2)(NO)]PF_6	2.204(5)	1.236(4)	1.236(4)	118.2(5)	0.061	a	265

Monodentate nitrito complexes

Complex	Bond length M–L (Å)	∠MON (°)	Bond length N–O (Å)		∠ONO (°)	R factor	Comments	Ref.
$[Cr(py)_3(NO)(ONO)_2]\cdot py$	1.96(1)	115.0(7)	1.34(1)	1.13(1)	112(1)	0.059	b	21
$[Cr(NH_3)_5(ONO)]Cl_2$	–	–	–	–	–	0.120	d	257
$[Co(en)_2(ONO)(NCS)]I$	1.915(7)	115.1(6)	1.30(1)	1.24(1)	112.8(10)	0.054	a,b	214
$[Co(en)_2(ONO)(NCS)]ClO_4$	1.875(7)	115.0(6)	1.30(1)	1.25(1)	112.8(9)	0.081	a,b	214
$[Co(NH_3)_5(ONO)]Cl_2$	1.927(5)	131.3(9)	1.037(10)	1.244(9)	125.3(11)	0.050	d,e	2
Ni(NN'-dimen)$_2(ONO)_2$	2.113(2)	119.3(1)	1.288(3)	1.215(3)	115.1(2)	0.045	a,b	14
Ni(2-meim)$_4(ONO)_2$	2.05(2) 2.28(2)	123(2) 123(2)	1.11(4) 1.24(4)	1.27(3) 1.26(5)	123(3)	0.024	d,e	29
$Ni(py)_4(ONO)_2\cdot 2py$	2.048(6)	149(1)	1.05(2)	1.26(2)	123(2)	0.059	e	28
$Ni(pyr)_4(ONO)_2$	2.09(1) 2.14(1)	–	–	–	–	0.032	d,e	28
Ni(4-mepy)$_4(ONO)_2$	2.089(9) 2.092(9) 2.122(12) 2.081(10)	–	–	–	–	0.078	d,e	28
μoxo$[Ni(py)_3(ONO)]_2\cdot 2py$	2.085(5)	126.0(6)	0.978(7)	1.357(6)	117.8(7)	0.056	e	258
$[Cu_2(bipy)_2(MeO)(NO_2)_3]$	2.074(6)	118.8(5)	1.265(11)	1.174(11)	113.1(8)	0.048	a,b	249
$K_3[Cu(NO_2)_5]$	f	f	f		f	0.056	f	34
Zn(NN-dimen)$_2(ONO)_2$	2.221(3)	118.0(2)	1.302(5)	1.141(6)	114.6(3)	0.042	a,b	27
$[Ru(sal_2en)(ONO)(NO)]PF_6$	2.011	–	–	–	–	0.043	d	259

Chelated *OO′* nitrito groups

Complex	Bond length M–O (Å)		∠OMO (°)	Bond length N–O (Å)		∠ONO (°)	*R* factor	Comments	Ref.
Ni(*NNN′N′*-tetmen)$(O_2N)_2$	2.074(2)	2.138(2)	59.70(10)	1.258(4)	1.238(4)	113.0(3)	0.030	a,b	38
	2.065(2)	2.109(2)	59.97(8)	1.260(4)	1.235(4)	112.3(3)			
[Ni(2-meim)$_4$(O_2N)](NO_3)·$\frac{1}{2}$MeOH	2.148(5)	2.178(6)	57.3(2)	1.269(11)	1.250(9)	110.8(6)	0.045	a,b	29
[Ni(3-mepy)$_2$$(O_2N)_2$]$_3$·$C_6H_6$	2.144(3)	2.090(3)	59.2(1)	1.260(4)	1.261(5)	112.0(3)	0.038	a,b	43
[Ni(4-mepy)$_2$$(O_2N)_2$]$_2$·2$C_6H_6$	2.106(6)	2.106(6)	59.4(3)	1.25(1)	1.25(1)	113.2(6)	0.045	a,b	43
[Ni(bipy)$_2$(O_2N)]NO_3	2.132(5)	2.110(6)	59.2(2)	1.241(8)	1.262(8)	113.6(6)	0.060	a,b	167
[Ni(*NN′*-dieen)$_2$(O_2N)]NO_2	2.151(7)	2.155(7)	58.7(3)	1.266(10)	1.256(10)	113.8(7)	0.056	a,b	31
	2.153(7)	2.148(7)	58.5(3)	1.248(10)	1.259(10)	114.0(7)			
[Ni(*NN′*-dieen)$_2$(O_2N)]BF_4	2.099(3)		59.2(1)	1.258(7)		111.7(4)	0.053	a,b	40
[Ni(en)$_2$(O_2N)]NO_3	–		–	–		–	–		9
[Ni(en)$_2$(O_2N)]	–		–	–		–	–	d	260
[Cu(bipy)$_2$(O_2N)]NO_3	2.238(10)	2.329(10)	52.5(4)	1.23(1)	1.21(1)	112(1)	0.081	a,b	261
[Cu(bipy)$(O_2N)_2$]	1.986(10)	2.508(10)	54.2(4)	1.27(1)	1.22(2)	115(1)	0.075	a,b	37
	1.988(10)	2.477(9)	55.0(4)	1.27(2)	1.23(2)	115(1)			
[Cu(*NN′*-dieen)$(O_2N)_2$]	2.235(10)	2.509(12)	47.4(3)	1.235(28)	1.106(19)	110(2)	0.092	a,b	262
[Cu(*NN*-dieen)$(O_2N)_2$]	2.001(8)	2.424(10)	55.1(3)	1.240(15)	1.236(13)	114.3(11)	0.068	a,b	35
	2.012(8)	2.479(11)	54.5(3)	1.300(15)	1.232(14)	111.9(10)			
K_3[Cu$(NO_2)_5$]	f		f	f		f	0.056	f	34
Cu(*NNN′N′*-tetmen)$(O_2N)_2$	2.03(1)	2.40(1)	54.2(5)	1.26(2)	1.24(2)	115.0(16)	0.131	–	36
	2.00(1)	2.47(1)	56.1(6)	1.25(2)	1.23(2)	113.7(17)			
$Cs_2Zn(O_2N)_4$	2.085(20)	2.536(21)	53.7(7)	1.254(27)	1.299(29)	112.8(19)	0.103	–	45
[Zn(en)$_2$(O_2N)]NO_2	2.240(5)	2.240(5)	55.2(2)	1.234(6)	1.234(6)	114.4(6)	0.045	a,b	27
[Zn(en)$_2$(O_2N)]ClO_4	2.251(4)	2.274(4)	54.6(1)	1.248(6)	1.258(5)	111.7(4)	0.031	a,b	38
[Zn(*NNN′N′*-tetmen)$(O_2N)_2$]	2.072(2)	2.339(3)	55.90(9)	1.258(4)	1.260(3)	111.8(2)	0.029	a,b	38
	2.072(2)	2.265(2)	55.89(9)	1.267(4)	1.250(4)	112.0(2)			
K_3[Hg$(O_2N)_4$]NO_3	2.494(1)	2.414(1)	–	1.231(1)	1.248(1)	114.34(9)	0.034	a	46
	2.548(2)	2.548(2)	–	1.235(1)	1.235(1)	114.72(17)			
	2.566(2)	2.394(5)	–	1.232(2)	1.250(3)	114.84(15)			
Cd(en)$(O_2N)_2$	2.31(1)	2.37(1)	51.3(5)	1.25(3)	1.28(3)	106.5(15)	0.093	–	10
K_2[Cd$(O_2N)_4$]	2.385(17)	2.385(17)	53.6(6)	1.33(3)	1.33(3)	108.4(24)	0.131	–	45
	2.406(22)	2.406(22)	50.4(7)	1.26(3)	1.26(3)	109.1(24)			
	2.509(21)	2.390(18)	49.8(6)	1.23(3)	1.22(3)	115.1(20)			

(*N*,*O*)-Bridged nitrito groups

Complex	Bond lengths (Å)				∠ONO (°)	*R* factor	Comments	Ref.
	M–O	M–N	N–O					
$[Co(NO)_2(NO_2)]$	2.15	1.98	1.08	1.23	–	0.029	–	55
$[Ni(en)_2NO_2]_\infty(ClO_4)_\infty$	2.184(6)	2.172(6)	1.247(8)	1.218(8)	111.8(5)	0.056	d,e	38
$[(NH_3)_3Co(OH)(NO_2)_2Co(NH_3)_3]Cl_3\cdot H_2O$	1.923	1.905	1.290	1.212	114.7	0.106	–	189
	1.917	1.901	1.300	1.203	117.4			
$[Co_2(NH_3)_8(NH_2)(NO_2)]Cl_4\cdot 4H_2O$	1.896	1.915	1.307	1.227	113.7	0.048	a,b	48
$[Co_2(NH_3)_8(NH_2)(NO_2)]Cl_4\cdot 2H_2O$	1.933(4)	1.933(4)	1.307(7)	1.175(8)	112.24(4)	0.038	e	47
$[Co_2(en)_4(NO_2)(NH_2)](NO_3)_4$	–		–		–	–	d	263
$[Ni(3\text{-mepy})_2(NO_2)_2]_3\cdot C_6H_6$	2.070(2)	2.078(3)	1.259(3)	1.230(3)	115.6(3)	0.038	a,b	43
$[Ni(4\text{-mepy})_2(NO_2)_2]_2\cdot 2C_6H_6$	2.122(14)	2.122(14)	1.18(2)	1.19(2)	113.1(15)	0.045	b	43
$[Ni_5(en)_4(OH)_2(NO_2)_8]\cdot H_2O$	2.080(4)	2.135(6)	1.279(7)	1.227(7)	114.8(5)			
	2.088(5)	2.138(6)	1.258(8)	1.224(10)	115.2(6)			
	2.082(5)	2.102(1)	1.285(8)	1.220(8)	116.3(8)			
	2.138(5)	2.158(7)	1.343(10)	1.175(10)	113.3(6)	0.059	a,b	51
$[Cu_2(OMe)(bipy)_2(NO_2)_3]$	2.177(13)		1.408(13)	1.103(18)	105.2(11)	0.048	e	49

(*O*)-Bridged nitrito groups

Complex	Bond lengths (Å)				∠ONO (°)	*R* factor	Comments	Ref.
	M–O		N–O					
$[Co(NO)_8(NO_2)_2(N_2O_2)]$	2.009	1.976	1.354	1.199	112.9	0.060	e	56
$[Ni(3\text{-mepy})_2(NO_2)_2]_3\cdot C_6H_6$	2.079(2)	2.097(3)	1.305(4)	1.197(4)	114.4(2)	0.038	a,b	43
$[Ni_5(\textit{NN}\text{-dimen})_4(OH)_2(NO_2)_8]CH_3CN$	–		–	–	–	0.076	e	51
$[Ni(4\text{-mepy})_2(NO_2)_2]_2\cdot 2C_6H_6$	2.037(4)	2.037(4)	1.24(1)	1.17(1)	123.6(7)	0.045	e	43

[a] Nitrite defined accurately. [b] Nitrite dimensions used in the statistical analysis reported in section D. [c] Abnormally high thermal motion in non-coordinated nitrite atoms. [d] Insufficient data reported to determine the reliability of the nitrite dimensions. [e] Disorder or twinning present. [f] Contains twenty independent nitrite ions, bonded as monodentate nitro and nitrito, and chelating groups.

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