Benzoyl-β-alaninato Nickel(II) Complexes. The Amino Effect on the Amino Acid Coordination around the Nickel Ion

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A compound of the type Ni(Bz-β-ala)$_2$·2H$_2$O (Bz-β-ala=benzoyl-β-alaninate anion) and its amine adducts of the type Ni(Bz-β-ala)$_2$B$_n$·xH$_2$O (n=1; B=piperazine (pipz), 1,10-phenanthroline (*o*-phen) and x=2; n=1, B=2,2′-bipyridine (2,2′-bpy) and 4,4′-bipyridine (4,4′-bpy) and x=4; n=2, B=*N*-methylpiperazine (CH$_3$-pipz), morpholine (morph), pyridine (py), 3-methylpyridine (3-pic) and 4-methylpyridine (4-pic) and x=2; n=3, B=en, and x=0) were prepared. Each complex was characterized by elemental analysis, solid spectroscopy and magnetic moment. All the complexes are six-coordinated and the presence of NiO$_6$ and NiN$_6$ chromophores for Ni(Bz-β-ala)$_2$·2H$_2$O and Ni(en)$_3$(Bz-β-ala)$_2$ complexes respectively and of NiO$_4$N$_2$ chromophores for the amine adducts is suggested. In all the complexes the amino acid appears to act as a bidentate ligand toward the carboxyl group. A ligand field strength in the aromatic heterocyclic amine adducts was found greater than in the aliphatic heterocyclic amine adducts. The amine adducts complexes appear to dissociate in solution with a change of the donor site, without changing in the stereochemistry, around the nickel ion.

In the framework of a systematic investigation we have examined the interaction of small peptides, as *N*-acetyl-[1–3] and *N*-benzoylglycine[4,5] with some transition metal ions. A recent study deals with the interaction of the copper ion with the benzoyl-β-alanine and the effect of the amines on the coordination properties of the amino acid and on the geometry around the copper ion.[6]

This work treats the nickel complexes of the benzoyl-β-alanine and their amine adducts. The nickel(II) peptide complexes may be of great help in understanding the reactions and stereochemistries of the peptide complexes of other metals, and thus the coordination behavior of peptides in general. Further interest may be derived by the fact that nickel may also have a biological role in animals, as it is recently suggested.[7]

Experimental

Preparation of the Compounds. The Ni(Bz-β-ala)$_2$·2H$_2$O complex was prepared by mixing a potassium benzoyl-β-alaninate (2×10^{-2} mmol) solution in methanol with a nickel(II) perchlorate hexahydrate (1×10^{-2} mmol) in ethanol at room temperature. After cooling at 5 °C for one hour and filtering the potassium perchlorate precipitated, the solution was slowly evaporated until an oil was obtained. The oil was dissolved in acetone, treated with diethyl ether and cooled at 5 °C. After some days a microcrystalline pale-green compound separated from the solution. This nickel(II) salt was used as starting materials for the adduct preparation.

Ni(Bz-β-ala)$_2$B$_2$·2H$_2$O(B=py and morph). The compounds were obtained by dissolving the nickel salt (1 mmol) in 3—4 cm^3 of the amines, adding acetone (5 cm^3) and diethyl ether (5 cm^3) and cooling at 5 °C.

Ni(Bz-β-ala)$_2$B$_2$·2H$_2$O(B=3-pic, 4-pic and CH$_3$-pipz). The salts were prepared by dissolving the nickel salt (1 mmol) in the amines (5 cm^3), adding diethyl ether until an incipient precipitation was obtained and by cooling at 5 °C.

Ni(Bz-β-ala)$_2$B·xH$_2$O(B=pipz and o-phen and x=2; B=4,4′-bpy and x=4). The complexes were prepared by treating an ethanolic solution (5 cm^3) of the nickel salt (1 mmol) with an ethanolic solution (5 cm^3) of the amines (1.5 mmol), adding diethyl ether and cooling at 5 °C.

Ni(en)$_3$(Bz-β-ala)$_2$. Complex was prepared by suspending the nickel salt in ethanol (5 cm^3), adding en (1 cm^3) and warming the solution at 50—60 °C until a clear solution was obtained. By adding diethyl ether and cooling at 5 °C a crystalline compound precipitated.

Physical Measurments. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer in KBr pellets (4000—250 cm^{-1}) and in Nujol mull (600—250 cm^{-1}). The electronic spectra of the compounds were recorded with a Beckman DK 1A spectrophotometeter. Solid samples were prepared by grinding the complexes on a filter paper as support. The room-temperature magnetic moments were measured with Gouy method by using Ni(en)$_3$S$_2$O$_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants.

Analyses. Nitrogen, carbon and hydrogen were analyzed by Mr. Giuseppe Pistoni using a Perkin-Elmer 240 Elemental Analyser.

Results and Discussion

The prepared compounds and their colors, analyses and magnetic moments are reported in Table 1. All the complexes are stable in air and soluble in chloroform or methanol. From these solvents the compounds cannot be recrystallized, as the ligand precipitated by evaporation of the solutions.

Electronic and Magnetic Properties of the Complexes in the Solid State. The coordination geometry of the complexes reported in this paper is studied and discussed in the light of their electronic and magnetic properties.

The magnetic moments (Table 1) of all the complexes, which do not show significant change, passing from the (benzoyl-β-alaninato) nickel(II) dihydrate to its adducts with bases, indicate a high spin configuration, corresponding to a possible cubic or tetragonal symmetry.[8]

The electronic spectra of all the nickel complexes (Table 2) are typical of hexacoordinated nickel(II). The three absorption peaks in each spectrum indicate a rather symmetric octahedral field.[9] The low energy band is broad, but all the others are quite symmetrical.

Table 1. Analytical and magnetic data

		C%		H%		H%		μ_{eff}
		Calcd	Found	Calcd	Found	Calcd	Found	
$Ni(Bz\text{-}\beta\text{-}ala)_2 \cdot 2H_2O$	pale green	50.11	49.44	5.05	5.04	5.86	5.86	3.47
$Ni(Bz\text{-}\beta\text{-}ala)_2(pipz) \cdot 2H_2O$	pale green	50.97	50.47	6.07	6.50	9.92	10.11	3.43
$Ni(Bz\text{-}\beta\text{-}ala)_2(CH_3\text{-}pipz)_2 \cdot 2H_2O$	pale green	53.01	53.40	7.12	7.62	12.38	12.27	3.19
$Ni(Bz\text{-}\beta\text{-}ala)_2(morph)_2 \cdot 2H_2O$	pale green	51.44	51.80	6.48	6.82	8.58	8.37	3.22
$Ni(Bz\text{-}\beta\text{-}ala)_2(py)_2 \cdot 2H_2O$	light blue	56.51	56.23	5.38	5.46	8.80	9.09	3.31
$Ni(Bz\text{-}\beta\text{-}ala)_2(3\text{-}pic)_2 \cdot 2H_2O$	light blue	57.74	56.98	5.76	5.93	8.43	8.36	3.28
$Ni(Bz\text{-}\beta\text{-}ala)_2(4\text{-}pic)_2 \cdot 2H_2O$	light blue	57.74	57.69	5.76	5.89	8.43	8.62	3.22
$Ni(Bz\text{-}\beta\text{-}ala)_2(2,2'\text{-}bpy) \cdot 4H_2O$	pale green	53.65	52.96	5.41	5.45	8.35	9.10	3.28
$Ni(Bz\text{-}\beta\text{-}ala)_2(4,4'\text{-}bpy) \cdot 4H_2O$	light blue	53.65	54.27	5.41	5.39	8.35	8.24	3.47
$Ni(Bz\text{-}\beta\text{-}ala)_2(o\text{-}phen) \cdot 2H_2O$	pale green	58.27	57.82	4.89	4.87	8.50	8.73	3.25
$Ni(Bz\text{-}\beta\text{-}ala)_2(en)_3$	lilac	50.07	50.01	7.11	7.64	17.98	16.99	3.06

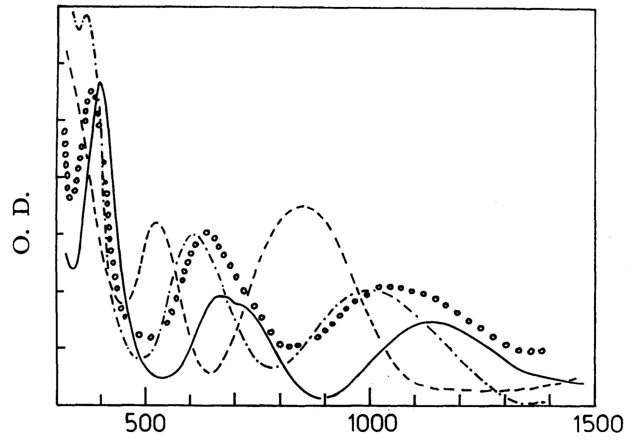

Fig. 1. Electronic spectra of the solid $Ni(Bz\text{-}\beta\text{-}ala)_2 \cdot 2H_2O$ (——); $Ni(Bz\text{-}\beta\text{-}ala)_2(morph)_2 \cdot 2H_2O$ (○○○○); $Ni(Bz\text{-}\beta\text{-}ala)_2(py)_2 \cdot 2H_2O$ (-·-·-) and $Ni(en)_3(Bz\text{-}\beta\text{-}ala)_2$ (- - -) complexes.

The band maxima of the absorption spectra in Table 2 are listed in order of increasing energy. The energy represents the eletronic transition from the $^3A_{2g}$ ground state to the successively higher excited states, $^3T_{2g}(\nu_1)$, $^1E_g(\nu_2)$, $^3T_{1g}(F)(\nu_3)$, and $^3T_{1g}(P)(\nu_4)$.

The dihydrate bis(benzoyl-β-alaninato)nickel(II) complex shows an electronic spectrum similar to that of the hexaaqua nickel(II) cation[10,11] indicating no difference in ligand field strength between the oxygens of the water and of the benzoyl-β-alanine.

On the other hand the tris(ethylenediamine)nickel(II) dibenzoyl-β-alaninato complex shows the typical spectrum of the tris(ethylenediamine)nickel(II) cation[11,12] suggesting the presence of the amino acids in the ionic form.

When the effect of additional binding of amine ligands on the electronic spectrum of the bis(benzoyl-β-alaninato)nickel(II) dihydrate (NiO_6 chromophore) was investigated, it was found that the d-d bands shift linearly to a shorter wavelength toward the position of the d-d bands found for the tris(ethylenediamine)-nickel(II) di-benzoyl-β-alaninato complex (NiN_6 chromophore). This may indicate that the adduct complexes have chromophore groups containing both the oxygen and nitrogen atoms, confirming the amine coordination. Spectra exemplifying this situation are reported in Fig. 1.

As the energy of the first band represents the average ligand field strength,[9] we found a greater ligand field effect in the aromatic heterocyclic amine adducts than in the aliphatic heterocyclic amine adducts.

Table 3 gives the wave numbers of the first band maximum of a series of nickel(II) and copper(II) complexes. The ratio between the observed wave numbers ν_{Cu}/ν_{Ni} gives a relative measure for the tetragonality of the copper complex and it was found that ν_{Cu}/ν_{Ni} varies from 1.1, in cases where the copper complexes approximate to cubic symmetry, to 1.7 in the cases of strong tetragonality.[13] The ν_{Cu}/ν_{Ni} values found for our adducts confirm that the copper adducts possess a strongly tetragonal distorted or square planar coordination as previously suggested.[6]

Infrared Spectra of the Complexes in the Solid State (Table 2). The assignment of the antisymmetric and symmetric carboxy stretching frequencies and of the CO ketonic and NH stretching frequencies of the benzoyl-β-alanine, which are considered very important in the assignment of the coordination sites on the amino acid, are made, as previously described,[6] by comparing the amino acid, its potassium salt and their deuterated analogues.

The peptide group is uncoordinated in all the complexes reported in this work, as in the case of the copper complexes,[6] as the shift to higher energies of the NH and CO ketonic stretching bands with respect to the free ligands suggests. These groups are however differently involved in some inter or intramolecular hydrogen bondings varying their position from 1640—1642 cm^{-1} $\nu(CO)_{ket}$ and 3400 cm^{-1} $\nu(NH)$ in the py, 3-pic and 4-pic adducts to 1618—1632 cm^{-1} $\nu(CO)_{ket}$ and 3400 cm^{-1} $\nu(NH)$ in the other complexes. This indicates lower hydrogen bonding interactions in the former complexes than in the latter.

IR-active $\nu(OCO)$ vibrations, associated with carboxylate ligands, RCO_2^-, give rise to bands in the region 1300—1700 cm^{-1}. Values of $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ for uni- or bi-dentate carboxylate ligands, RCO_2^-, are dependent upon the eletronic nature of the group R, the properties of the central metal ion, and

TABLE 2. ELECTRONIC AND INFRARED SPECTRA (cm^{-1}) ON THE COMPLEXES IN THE SOLID STATE[a)]

	ν_1	ν_2	ν_3	ν_4	ν(NH)	ν(NH)^B	ν(CO)$_{ket}$	ν(OCO)$_a$	ν(OCO)$_s$	$\Delta\nu$
Ni(Bz-β-ala)$_2$·2H$_2$O	8810(17)	13510 sh(16)	14930(21)	25970(62)	3330 vsb		1625 vs	1562 vs	1404 vs	158
Ni(Bz-β-ala)$_2$·pipz·2H$_2$O	9430(12)		15630(39)	26320(114)	3347 m 3300 sh	3222 m 3180 sh	1625 vs	1560 vs	1400 s	160
Ni(Bz-β-ala)$_2$(CH$_3$-pipz)$_2$·2H$_2$O	9850(10)		16260(14)	27400(45)	3358 s	3232 s	1618 vs	1523 vs	1398 vs	125
Ni(Bz-β-ala)$_2$(morph)$_2$·2H$_2$O	9710(15)		15870(24)	26880(53)	3340 sb	3260 m 3200 vs	1632 vs	1530 vs	1390 vs	140
Ni(Bz-β-ala)$_2$(py)$_2$·2H$_2$O	10000(20)		16260(30)	28170(68)	3402 m		1642 vs	1512 vs	1393 vs	119
Ni(Bz-β-ala)$_2$(3-pic)$_2$·2H$_2$O	10100(15)		16530(25)	27770(48)	3404 m		1640 vs	1510 vs	1390 vs	120
Ni(Bz-β-ala)$_2$(4-pic)$_2$·2H$_2$O	9950(12)		16260(18)	27400(42)	3408 m		1642 vs	1507 vs	1388 vs	119
Ni(Bz-β-ala)$_2$(2,2′-bpy)·4H$_2$O	10310(29)		16130(35)	26320 sh(68)	3390 mb		1625 vs	1558 vs	1412 s	146
Ni(Bz-β-ala)$_2$(4,4′-bpy)·4H$_2$O	9900(21)		16340(46)	27030 sh(150)	3320 sb		1630 s	1588 vs	1402 sb	186
Ni(Bz-β-ala)$_2$(*o*-phen)·2H$_2$O	10200(19)		16130(24)	27400 sh(150)	3390 mb		1625 vs	1558 vs	1412 s	146
Ni(en)$_3$(Bz-β-ala)$_2$	11760(37)		18350(35)	28570 sh(135)	3300 s	3275 sh 3230 sh 3135 m	1625 vs	1550 vs	1382 vs	168

a) Optical density in arbitrary scale are reported in parenthesis.

TABLE 3. FIRST ABSORPTION BAND (cm^{-1}) OF SEVERAL NICKEL(II) AND COPPER(II) COMPLEXES
The ratio ν_{Cu}/ν_{Ni} gives a measure of the tetragonality effects.

Complex	ν_{Ni}	ν_{Cu}	ν_{Cu}/ν_{Ni}	Complex	ν_{Ni}	ν_{Cu}	ν_{Cu}/ν_{Ni}
(Bz-β-ala)$_2$(pipz)	9430	16950	1.80	(Bz-β-ala)$_2$(4-pic)$_2$	9950	16130	1.62
(Bz-β-ala)$_2$(CH$_3$-pipz)$_2$	9850	15630	1.59	(Bz-β-ala)$_2$(2,2′-bpy)	10310	15870	1.54
(Bz-β-ala)$_2$(morph)$_2$	9710	16000	1.65	(Bz-β-ala)$_2$(4,4′-bpy)	9900	16000	1.62
(Bz-β-ala)$_2$(py)$_2$	10000	16130	1.61	(Bz-β-ala)$_2$(*o*-phen)	10200	10530 13510	1.03

TABLE 4. ELECTRONIC AND INFRARED SPECTRA (cm^{-1} AND ε/l mol^{-1} cm^{-1} (in parentheses)) OF THE COMPLEXES IN SOLUTION[a)]

		ν_1	ν_2	ν_3	ν_4	ν(NH)	ν(NH)^B	ν(CO)$_{ket}$	ν(OCO)$_a$	ν(OCO)$_s$	$\Delta\nu$
Ni(Bz-β-ala)$_2$·2H$_2$O	MeOH	8930(6)	13700 sh(4)	15270(4)	25640(10)						
Ni(en)$_3$(Bz-β-ala)$_2$	MeOH	11560(7)		18690(7)	29850(19)						
Ni(Bz-β-ala)$_2$(CH$_3$-pipz)$_2$·2H$_2$O	CHCl$_3$	8700(7)	13510 sh(5)	15150(7)	25640(19)	3400 sh	3310 mb		1632 vs	1410 s	222
	CHCl$_3$+CH$_3$-pipz			15630(9)	26320(24)	3410 sh	3318 s		1638 vs	1410 sh	228
Ni(Bz-β-ala)$_2$(morph)$_2$·2H$_2$O	CHCl$_3$	8700(7)	13510 sh(5)	15130(7)	25640(17)	3400 sh	3300 mb		1630 vs	1410 vsb	220
	CHCl$_3$+morph		13330 sh(5)	15380(9)	25840(24)	3415 sh	3315 s		1638 vs	1410 sh	228
Ni(Bz-β-ala)$_2$(py)$_2$·2H$_2$O	CHCl$_3$	9260(8)	13610 sh(4)	16000(9)	26670(17)	3350 mb		1635 s	1592 vs	1408 vs	184
	CHCl$_3$+py	9430(8)	13610 sh(4)	16070(9)	26880(17)	3400 sh 3330 ms		1635 s	1590 vs	1403 s	187
Ni(Bz-β-ala)$_2$(3-pic)$_2$·2H$_2$O	CHCl$_3$	9170(8)	13510 sh(5)	15870(9)	26320(18)	3400 sh 3325 m		1638 s	1590 vs	1412 vs	178
	CHCl$_3$+3-pic	9480(8)	13420 sh(4)	16000(10)	25640(19)	3380 sh 3325 m		1638 s	1588 vs	1408 vs	180
Ni(Bz-β-ala)$_2$(4-pic)$_2$·2H$_2$O	CHCl$_3$	9170(8)	13510 sh(4)	15920(9)	26320(18)	3365, 3325 m		1638 s	1592 vs	1415 s	177
	CHCl$_3$+4-pic	9520(9)	13510 sh(4)	16130(11)	26880(22)	3400 sh 3322 s		1638 s	1600 vs	1409 s	191

a) The solution electronic and infrared spectra have identical concentration: (2.10—3.20)×10^{-2} M.

possibly the identity of the *trans*-ligands present.[14)]

The values of $\nu(OCO)_{asym}$ and the $\Delta\nu$ separation ($\nu(OCO)_{asym}-\nu(OCO)_{sym}$) afford the most sensitive indication of the mode of carboxylate coordination. Bidentate carboxylate has values of $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ close to those found in the corresponding free ion whereas unidentate carboxylate has $\nu(OCO)_{asym}$ at substantially higher frequencies and thus give larger values of $\Delta\nu$.[14,15)] Our assignment of uni- or bi-dentate carboxylate group is based on these criteria.

The reported values of $\Delta\nu$ for the $Ni(en)_3(Bz\text{-}\beta\text{-}ala)_2$ complex of 168 cm^{-1} are assumed to typify ionic benzoyl-β-alaninate spectra, for which the values of $\Delta\nu$, found in all the complexes lower than 168 cm^{-1}, may indicate the presence of bidentate carboxyl groups. In the py, 3-pic and 4-pic and CH_3-pipz adducts in which the $\Delta\nu$(119—125 cm^{-1}) is strongly reduced compared with the ionic values, it may suggest that both benzoyl-β-alaninato ions act as symmetrical chelates.[16)]

The highest values of $\Delta\nu$ are found for the pipz (160 cm^{-1}) and 4,4′-bpy (186 cm^{-1}) adducts. These ligands which cannot be bidentate, but have two donor sites, must therefore bind with different nickel ions giving rise to polymeric complexes. This is supported by their insolubility, by the similar behavior exhibited in other amino acid adducts.[6)] The coordination of the amines is confirmed by the shift to lower frequencies of the $\nu(NH)^{B}$ (Table 2) in the aliphatic heterocyclic amine adducts and by the shift of the bands in the 800—500 cm^{-1} region in the aromatic heterocyclic amine adducts by respect to the free amines.[6)] In the en complex the position of the $\nu(NH)^{B}$ bands is consistent with a bidentate coordination of the ethylenediamine.[17)]

Since the amino acid acts as chelating agent and the amines turn out to be clearly coordinated to the metal ion, we may exclude the presence of coordinated water in all the amine adducts.

These results and the position of the d-d bands in all the amine adducts are consistent with the presence of N_2O_4 donor sets.

Electronic and Infrared Spectra of the Complexes in Solution (Table 4). The electronic spectra of all the complexes in solution moreover suggest the presence of hexacoordinated nickel(II). While the solution eletronic spectra of the $Ni(Bz\text{-}\beta\text{-}ala)_2\cdot 2H_2O$ and $Ni(en)_3(Bz\text{-}\beta\text{-}ala)_2$ complexes in methanol resemble those of the solid complexes, those of the other adducts show a red shift of the d-d bands compared with those of the corresponding solid compounds greater in chloroform in presence of an amine excess. The band at 3310 and 3300 cm^{-1} in the $Ni(Bz\text{-}\beta\text{-}ala)_2\cdot B_2\cdot 2H_2O$ ($B=CH_3$-pipz and morph), respectively, which is enhanced in intensity in presence of amine excess, may indicate the presence of uncoordinated amine. The $\nu(OCO)_{asym}$ position (1630—38 cm^{-1}) and the $\Delta\nu$ separation (220—228 cm^{-1}) in these complexes are similar to those found for the benzoyl-β-alaninato copper complexes and other copper complexes having dimeric carboxylate structure.[6)] This may suggest that the carboxylate group acts as dimeric bidentate or bridging unidentate ligand. The hypothesis of a copper acetate monohydrate type coordination cannot be supported by magnetic measurements in solution, these complexes being insufficiently soluble.

Instead, an essentially unidentate coordination of the amino acid may be proposed for the aromatic heterocyclic amine adducts in chloroform solution from the $\nu(OCO)_{asym}$ position (1588—1600 cm^{-1}) and from the $\Delta\nu$ separation (177—191 cm^{-1}). Their electronic spectra are still consistent with a NiO_4N_2 chromophore, suggesting that the two coordination positions lost from the carboxylate groups may be replaced by water molecules.

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References

1) G. Marcotrigiano and G. C. Pellacani, *Inorg. Nucl. Chem. Lett.*, **11**, 643 (1975).

2) G. Marcotrigiano and G. C. Pellacani, *Can. J. Chem.*, **52**, 3607 (1974).

3) G. Marcotrigiano and G. C. Pellacani, *Z. Anorg. Allg. Chem.*, **415**, 268 (1975).

4) G. Marcotrigiano and G. C. Pellacani, *Z. Anorg. Allg. Chem.*, **413**, 171 (1975).

5) G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *J. Inorg. Nucl. Chem.*, **37**, 2344 (1975).

6) G. Marcotrigiano, L. Menabue, and G. C. Pellacani, *Inorg. Chim. Acta*, **19**, 133 (1976).

7) N. E. Dixon, C Gazzola, R. L. Blakeley, and B. Zerner, *J. Am. Chem. Soc.*, **97**, 4131 (1975).

8) A. B. P. Lever, *Inorg. Chem.*, **4**, 763 (1965).

9) R. S. Drago "Physical Methods in Inorganic Chemistry," Reinhold, New York, N. Y. (1965), Chap. 6.

10) L. Sacconi, *Trans. Metal. Chem.*, **4**, 199 (1968).

11) A. B. P. Lever "Inorganic Electronic Spectroscopy," Elsevier, New York (1968), p. 334.

12) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).

13) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

14) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," J. Wiley, New York (1963) and references cited therein.

15) S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, **1973**, 1912, and references cited therein.

16) N. W. Curtis, *J. Chem. Soc., A*, **1968**, 1579.

17) W. Berg and K. Rasmussen, *Spectrochim. Acta*, **29A**, 319 (1973).