ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 28

PERCHLORATE ION COMPLEXES

N. M. N. GOWDA, S. B. NAIKAR, and G. K. N. REDDY

Department of Chemistry, Central College, Bangalore University, Bangalore, India

I. Introduction 255
II. Perchlorate Ion Coordination and Methods of Identification 256
  A. X-Ray Crystal Structure Analysis 256
  B. Infrared and Raman Spectra 257
  C. Electronic Spectra. 258
  D. Magnetic Susceptibility and ESR Spectra 260
  E. Molar Conductivities. 260
III. Complexes of Early Transition Metals 260
IV. Complexes of Iron Group Metals 263
V. Complexes of Cobalt Group Metals 265
VI. Complexes of Nickel Group Metals 268
VII. Complexes of Copper Group Metals 273
VIII. Complexes of Zinc Group Metals 283
IX. Complexes of Lanthanides 287
X. Complexes of Other Metals 288
XI. Conclusion 290
XII. Abbreviations 291
References 294

I. Introduction

Coordination of perchlorate to transition and nontransition metal ions has been well established, though in most of the cases the metal–perchlorate bond is rather weak and has been termed as "semicoordination" (*1*). The coordination that can be recognized in the solid state may frequently break down in solution, particularly in aqueous medium (the solvent molecule replacing the coordinated perchlorate).

A concise survey of perchlorate complexes was made by Rosenthal (*2*) in 1973. A year later, the possibility of perchlorate coordination in aqueous medium was reviewed by Johansson (*3*). Since the publication of these two accounts a number of papers reporting new findings on perchlorate complexes have appeared, justifying another comprehen-

ISBN 0-12-023628-1

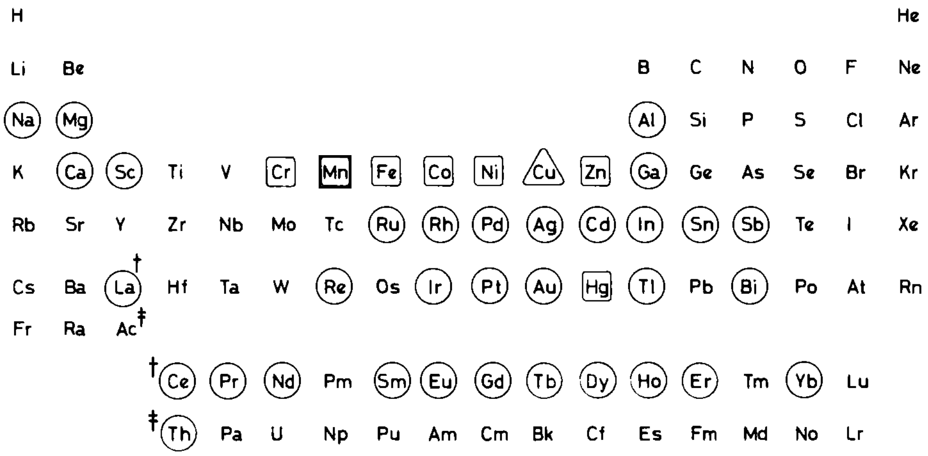


FIG. 1. Perchlorate ion complexes known: ○, a few; □, considerable; △, a large number.

sive review such as the one presented here. In this article only such perchlorate complexes where, in addition to perchlorate, at least another ligand (other than perchlorate) is also present, are considered. Figure 1 depicts the metals for which perchlorate complexes have been isolated.

II. Perchlorate Ion Coordination and Methods of Identification

The highly symmetrical perchlorate ion is a hard base and falls into the category of relatively nonpolarizable and noncoordinating anions such as BF_4^- and PF_6^- (*4*). Its ability to coordinate strongly to soft metal ions is therefore limited. When coordination does occur, the perchlorate group may be linked to a metal ion in a monodentate and/or bidentate manner through oxygen atoms (Fig. 2); the latter linkage can be either chelating (linked to the same metal ion) or bridging (bonded to two metal ions).

A. X-RAY CRYSTAL STRUCTURE ANALYSIS

X-ray crystal structure analysis has unequivocally established coordination of perchlorate in a number of perchlorate complexes. The O—Cl bond length of the coordinated part is generally greater than

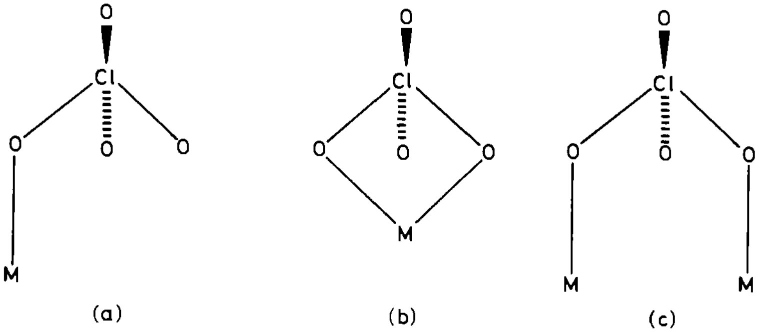


FIG. 2. Types of metal–perchlorate bonding: (a) monodentate; (b) chelating bidentate; (c) bridging bidentate.

that of the uncoordinated ones. The metal–perchlorate linkage is also manifest in the M—O—Cl bond angle, which is expected to be around 120° (*5, 6*), assuming that the coordinated oxygen uses sp^2 hybrid orbitals for bonding. The magnitude of the bond angle should give an idea of the metal–oxygen bond strength.

As early as 1965 Pauling *et al.* (*7*) and Cotton and Weaver (*8*) recognized coordinated perchlorate(s) in cobalt(II) complexes by X-ray structure analysis. In 1971, crystallographic evidence was presented by Nakai (*9*) to show that bridging, because of coordination by perchlorate, was responsible for the polymeric nature of $Cu(bipy)_2(ClO_4)_2$. Similarly, Hodgson and co-workers (*10*) identified the presence of intramolecular bidentate perchlorate in α-[Cu(dmaep)(μ-OH)(μ-ClO_4)$]_2$. The presence of both unidentate and chelating bidentate perchlorate groups in a few lanthanide complexes has clearly been established by Ciampolini *et al.* (*11*). There have been several other reports on the X-ray crystal structure analyses of perchlorate complexes. The recorded metal–perchlorate distances vary over a wide range even for the same metal ion, depending on the other ligands present and the geometry of the complex and indicating varying degrees of metal–oxygen interaction. The M—O bond length in copper complexes, for instance, ranges from 2.2 to 2.9 Å (p. 274). There are a few instances where the M—O distances are comparable to the sum of the covalent radii (*11–14*).

B. INFRARED AND RAMAN SPECTRA

Hathaway and Underhill (*15*) were the earliest to suggest the use of IR and Raman spectroscopic methods to investigate perchlorate coordination to a metal ion. Perchlorate ion with its T_d symmetry should have its nine vibrational degrees of freedom distributed among four normal modes of vibration; the assignments of these modes are collected in Table I. While all four vibrations, ν_1 to ν_4, of ClO_4^- are Raman active, only the triply degenerate frequencies ν_3 and ν_4 are IR active. The ν_3 band appears prominently in the IR as a very strong and broad band with a poorly defined maximum.

Monodentate attachment to a metal ion lowers the symmetry of perchlorate to C_{3v} and bidentate attachment to C_{2v} (*15–17*). Consequently the number of vibrational modes should increase (Table I). In addition, a metal–oxygen stretching frequency would also be expected in the far-IR region and has been located in the range 360–290 cm^{-1} (*18*). These effects resulting on coordination, particularly the increase in the number of vibrational modes, may be used for identifying coordination of perchlorate.

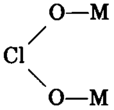
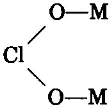
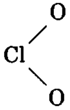
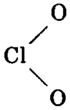
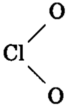
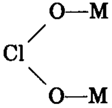
It must, however, be borne in mind that minor shifts and weak splittings of the IR bands may arise on account of lowering of site symmetry because of strong lattice effects or of coupling of vibrations between perchlorate groups or from a purely isotopic effect within the group (*15, 16*). For example, the broad and strong band due to the ν_3 mode of ionic perchlorate is often split because of lattice effects. Despite these limitations, with a little care and caution, coordinated and noncoordinated perchlorate(s) are conveniently identified by IR spectroscopy.

C. ELECTRONIC SPECTRA

Since the nature of the ligand field around the metal ion is often reflected in the spectral features, perchlorate coordination in a metal complex may also be revealed by the electronic spectra of the complex. For instance, in chromium(III) complexes, $CrL_4(ClO_4)_3$ (L = *n*-Bu_3PO, Ph_3PO, mmpp), the spectral bands around 460 and 650 nm are assigned to $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ transitions, respectively, arising from an octahedral stereochemistry for the complex requiring coordination of two of the perchlorates to the metal ion (*18–21*). The fact that both Ni(2-*i*-PrIm)$_4$(ClO_4)$_2$ and Ni(2-*i*-PrIm)$_4$I(ClO_4) show a band around 23,700 cm^{-1} (*22*) suggests that the ligand field strength of perchlorate is comparable to that of iodide. However, a few other reports (*12, 23*) have indicated the position of perchlorate to be very close to chloride in the spectrochemical series. The spectrochemical series for the anions represented by X in the complexes [NiX(tdaa)]ClO_4 is found to be (X =) I < Br < Cl < NO_3 < ClO_4 < NCS < CN, based on their electronic spectra (*24*).

TABLE I

NORMAL MODES OF VIBRATION OF PERCHLORATE

<table>
<tr><th>State of ClO_4^-
(symmetry)</th><th colspan="7">Vibration type and infrared and Raman activity[a,b]</th></tr>
<tr><td>Ionic
(T_d)</td><td>ν_1
A_1(R)
sy. str.
(940–925)</td><td colspan="2">ν_2
E(R)
sy. bend
(480–455)</td><td colspan="2">ν_3
T_2(IR,R)
asy. str.
(1100–1070)</td><td colspan="2">ν_4
T_2(IR,R)
asy. bend
(635–615)</td></tr>
<tr><td>Monodentate
(C_{3v})</td><td>ν_2
A_1(IR,R)
ClO str.
(950–870)</td><td colspan="2">ν_6
E(IR,R)
rocking
(480–460)</td><td>ν_1
A_1(IR,R)
ClO_3
sy. str.
(1040–1025)</td><td>ν_4
E(IR,R)
ClO—M
asy. bend
(1160–1020)</td><td>ν_3
A_1(IR,R)
ClO_3
sy. bend
(660–630)</td><td>ν_5
E(IR,R)
ClO_3
asy. bend
(620–600)</td></tr>
<tr><td>Bidentate
(C_{2v})</td><td>ν_2
A_1(IR,R)

sy. str.
(990–900)</td><td>ν_4
A_1(IR,R)

sy. bend
(480–450)</td><td>ν_5
A_2(R)
torsion
(440–400)</td><td colspan="2">ν_1
A_1(IR,R)

sy. str.
(1060–1020)</td><td colspan="2">ν_3
A_1(IR,R)

sy. bend
(670–635)</td></tr>
<tr><td></td><td></td><td></td><td></td><td>ν_6
B_1(IR,R)

asy. str.
(1140–1090)</td><td>ν_8
B_2(IR,R)

asy. str.
(1220–1140)</td><td>ν_7
B_1(IR,R)
rocking
(635–620)</td><td>ν_9
B_2(IR,R)
rocking
(620–605)</td></tr>
</table>

---

[a] sy. = symmetric; asy. = asymmetric; str. = stretching; bend. = bending; A, B = nondegenerate; E = doubly degenerate; T = triply degenerate; approximate vibrational frequency ranges (cm^{-1}) are given in parentheses.

[b] Taken by permission from B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.* 3091 (1961); R. P. Scholer and A. E. Merbach, *Inorg. Chim. Acta* **15,** 15 (1975).

D. MAGNETIC SUSCEPTIBILITY AND ESR SPECTRA

The coordination number of the metal ion, the stereochemistry of the complex, and hence the magnetic susceptibility may vary, depending on whether or not the perchlorate is coordinated to the metal ion. Thus magnetic susceptibility measurement can be of diagnostic value in determining the presence of the metal–perchlorate linkage. For example, the complex $Co(\beta\text{-PyBzl})_4(ClO_4)_2$ has a magnetic moment of 4.9 μ_B, suggesting octahedral stereochemistry for the complex and hence coordination of both perchlorates to the metal ion (*25*). Similarly the ligand field environment around a metal ion is reflected in the ESR spectrum of a complex and hence can be used to identify metal–perchlorate bonding (*26, 27*).

E. MOLAR CONDUCTIVITIES

Perchlorate coordinated to a metal ion in the solid state generally is displaced in a polar solvent by a solvent (or another ligand) molecule. However, under favorable conditions, perchlorate coordination may persist in solution. In such cases, conductivity measurements are helpful in detecting the coordination of perchlorate (*28*). For instance, the conductance values of some lanthanide complexes $Ln(hmpa)_4(ClO_4)_3$ (Ln = La, Nd, Gd, Dy, Yb) in nitrobenzene correspond to those of uni-univalent electrolytes, implying coordination of two of the perchlorates (*29*). The coordinated perchlorates are, however, easily displaced by the addition of hmpa as shown by the conductance values, which gradually increase to that corresponding to a 1:3 electrolyte.

III. Complexes of Early Transition Metals

Except for the scandium group, investigations on perchlorate complexes of the early transition metals, namely, the titanium and vanadium groups, appear not to have been carried out. Scandium perchlorate reacts with Ph_3PO in ethanol to give white crystals of composition $Sc(Ph_3PO)_4(ClO_4)_3$. On the basis of IR data, a distorted octahedral geometry with two monodentately coordinated perchlorates has been postulated for the complex. However, the complex is a 1:3 electrolyte in MeCN, $MeNO_2$, and dmf, owing to solvolysis (*30*). Treatment of lanthanum perchlorate in EtOH–teof (or dmp) with hmpa produced $La(hmpa)_4(ClO_4)_3$. Based on IR (Table II) and conductivity data, monodentate coordination of two of the perchlorates has been postulated

(*29*). However, the complex shows a band at 436 cm^{-1} in the Raman (it is absent in the IR) spectrum, which has been assigned to the ν_5 mode of bidentate perchlorate. Hence the lanthanide ion has been suggested to have a coordination number between six and eight (*17*). The La(III) ion attains coordination number 10 in $La(tmp)_7(H_2O)_2(ClO_4)_3$, with one of the perchlorates coordinated to the metal ion as indicated by the perchlorate band splittings in the IR. The complex behaves as a 1 : 2 electrolyte in $MeNO_2$, supporting the above deductions (*28*). The X-ray crystal structure analysis of $La(tdod)(H_2O)(ClO_4)_3$ has indicated a dec-atetrahedral geometry for the complex, with the metal ion attaining a coordination number of 10 (*31*). Two of the perchlorates are bound to the metal ion, one as a monodentate ligand (La—O = 2.494 Å) and the other as a bidentate ligand (La—O = 2.683, 2.738 Å). Similarly, the metal ion in $La(tdhc)(ClO_4)_3$ is contemplated to be 10-coordinate with two perchlorates behaving as unidentate and the third one as a bidentate ligand (*11*).

Karayannis and co-workers (*18–21, 32–36*) have reported the syntheses of paramagnetic, green chromium(III) perchlorate complexes of the compositions $CrL_4(ClO_4)_3$ (L = *n*-Bu_3PO, Ph_3PO, mmpp, ttp) and $CrL_2S_2(ClO_4)_3$ (L = tetp; S = H_2O; L = adHNO, puHNO; S = EtOH). Chromium(III) complexes are, in general, six-coordinate, and therefore two of the perchlorates in each of the above complexes would be acting as monodentate ligands. This is supported by the IR spectra (Table II) of the complexes. Bidentate nature of perchlorate is observed in the six-coordinate complex $Cr(depf)_2ClO_4$ (*37*). Perchlorate coordination has also been recognized in a variety of six-coordinate chromium(III) complexes containing *N*-oxides such as miqNO, phzNO, $phzNO_2$, quxNO, and $quxNO_2$ (*38–41*). The existence of $[Cr(H_2O)_5OClO_3]^{2+}$ ion in perchloric acid medium has been detected spectrophotometrically (*42*). A trinuclear complex of composition $[Cr_3(Ph_3PO)_8(OClO_3)_3](ClO_4)_6$ is also known (*20*).

Wimmer and Snow (*43, 44*) have prepared a few octahedral manganese(I) carbonyl complexes of the formulas $Mn(CO)_5OClO_3$ and $Mn(CO)_3L_2(OClO_3)$ (L = Ph_3P, $(PhO)_3P$; L_2 = bipy) by treating the corresponding bromides with $AgClO_4$ in dichloromethane. The pentacarbonyl undergoes substitution of perchlorate with Q (Ph_3P, *m*-$tolyl_3P$, *p*-$tolyl_3P$, dppe, dppm, MeCN, PhCN, Py, H_2O) to produce $[Mn(CO)_5Q]ClO_4$ complexes. Manganese(II) complexes of the type $MnL_4(ClO_4)_2$ (L = Me_3PO, Ph_3PO, Me_3AsO, Ph_3AsO, Ph_2MeAsO, MeCN, Py, 4-MePy, pyzNO, dpNO) have been reported (*15, 26, 45–50*). In the tertiary arsine oxide and phosphine oxide complexes, Mn has been postulated to have coordination number 5 on the basis of IR

TABLE II

PERCHLORATE FREQUENCIES OF EARLY TRANSITION METAL COMPLEXES

	Perchlorate bands (cm^{-1})				
Complex	ν_3	ν_1	ν_4	ν_2	Reference
$[Sc(Ph_3PO)_4(OClO_3)_2]ClO_4$	1190, 1082, 1068, 1022, 1015, 994	930, 895	623, 610	445	*30*
$[La(hmpa)_4(OClO_3)_2]ClO_4$	1119, 1112, 1099	916	644, 623, 614	480, 346^a	*29*
$[Cr(n\text{-}Bu_3PO)_4(OClO_3)_2]ClO_4$	1150, 1030	930	642, 616, 600	480, 460, 337^a	*18*
$[Cr(mmpp)_4(OClO_3)_2]ClO_4$	1125, 1090, 1039	923	652, 634, 618	327^a	*21*
$[Cr(miqNO)_4(H_2O)OClO_3]ClO_4$	1118, 1098, 1035		640, 629, 621, 616, 611	322^a	*38*
$Cr(depf)_2(O_2ClO_2)$	1212, 1115, 1030	932	655, 633	480, 460, 355^a	*37*
$Mn(CO)_5(OClO_3)$	1161, 1020	880	625		*43*
$Mn(CO)_3bipy(OClO_3)$	1146, 1021	884	633, 615		*43*
$Mn(CO)_3(Ph_3P)_2(OClO_3)$	1148, 1021	890	625		*43*
$[Mn(Ph_3PO)_4(OClO_3)]ClO_4$	1099, 1044	925	621, 614		*26*
$[Mn(miqNO)_5(OClO_3)]ClO_4$	1114, 1110, 1088, 1045		639, 628, 621, 614	284^a	*38*
$Mn(Py)_4(OClO_3)_2$	1130, 1030	936	625, 617		*47*
$Mn(qun)_2(O_2ClO_2)_2$	1107, 1090	937	633, 622	484	*47*
$[Mn(bdpm)_2(O_2ClO_2)]ClO_4$	1155, 1100, 1035	935	627, 619, 615		*51*
$Re(CO)_5(OClO_3)$	1190, 1162, 1150, 1021	910, 870	630		*54*
$Re(CO)_3bipy(OClO_3)$	1150, 1010	855	630		*54*

^{a} $\nu[M{-}O(ClO_4)]$.

spectra, which indicate coordination of one of the perchlorates to the metal ion. ESR spectral study of the above complexes (L = Ph_3PO, Ph_3AsO) also indicates five-coordination for the metal ion. Comparison with the ESR data of the analogous complexes MnL_4X_2 (X = I, NCS) suggests that the ligand field strength of perchlorate is comparable to that of iodide and isothiocyanate (*26*).

The electronic spectral results for the complex $Mn(qun)_2(ClO_4)_2$ are in consonance with a distorted octahedral environment around the metal ion, and as a consequence the perchlorates are bidentate (*47*); the IR spectrum of the complex, however, does not provide supporting evidence (Table II). On the other hand, bidentate behavior of one of the perchlorates in the $Mn(bdpm)_2(ClO_4)_2$ complex has been revealed by IR data (*51*). Infrared spectral measurements suggest the presence of both monodentate and ionic perchlorates in several manganese(II) complexes possessing such ligands as adHNO, miqNO, phzNO, $phzNO_2$, quxNO, $quxNO_2$, and adH (*34, 38–40, 52, 53*).

The six-coordinate $Re(CO)_3(bipy)OClO_3$ and $Re(CO)_5OClO_3$ are probably the only perchlorate complexes that are known for rhenium. They are prepared by treating the respective bromides with $AgClO_4$ in dichloromethane (*54*).

IV. Complexes of Iron Group Metals

Ferrous and ferric complexes of the formulas $FeL_4(ClO_4)_2$ (L = Me_3PO, *n*-Bu_3PO, Me_3AsO, miqNO) and $FeL_4(ClO_4)_3$ (L = *n*-Bu_3PO, Ph_3AsO, tetp, ttp, miqNO) have been reported (*18, 19, 32, 36, 38, 45, 55*). They are all paramagnetic and in most of them the metal ion is six-coordinate with two monodentately bound perchlorates as per the IR evidence (Table III). In a few of these complexes (L = Me_3PO, Me_3AsO, Ph_3AsO, miqNO), however, the metal ion is five-coordinate with a monodentate perchlorate. The electrical conductivity of many of these complexes, measured in nonaqueous polar solvents, suggests partial to complete replacement of coordinated perchlorates by solvent molecules. Ferrous perchlorate reacts with bdpm to produce the six-coordinate $Fe(bdpm)_2(ClO_4)_2$ complex wherein both the perchlorates are monodentate (*51*).

Reed *et al.* (*12*) and Masuda *et al.* (*56*) have elucidated the structures of five-coordinate iron(III) complexes $Fe(tpp)ClO_4$ (Fig. 3) and $Fe(oep)ClO_4$ by X-ray crystallography. In both complexes, the perchlorate is linked to the metal ion through one of the oxygen atoms at the apical site of the square pyramid. The Fe—O distance is slightly shorter in

TABLE III

PERCHLORATE FREQUENCIES OF IRON COMPLEXES

Complex	Perchlorate bands (cm^{-1})				Reference
	ν_3	ν_1	ν_4	ν_2	
$[Fe(miqNO)_4OClO_3]ClO_4$	1120, 1110, 1086, 1043		640, 629, 621, 614	326[a]	*38*
$Fe(n\text{-}Bu_3PO)_4(OClO_3)_2$	1150, 1030	930	640, 620, 602	480, 460, 290[a]	*18*
$Fe(bdpm)_2(OClO_3)_2$	1115, 1050	930			*51*
$[Fe(mmpp)_2(H_2O)_2OClO_3]_2(ClO_4)_2$	1145, 1100, 1034	920	639, 627, 613	295[a]	*21*
$[Fe(pyzNO)_3(H_2O)OClO_3]ClO_4$	1098, 1094	930	621	278[a]	*49*
$[Fe(n\text{-}Bu_3PO)_4(OClO_3)_2]ClO_4$	1140, 1030	910	635, 619, 599	480, 455, 315[a]	*18*
$[Fe(tetp)_4(OClO_3)_2]ClO_4$	1142, 1079, 1044	923	655, 637, 624		*32*
$[Fe(ttp)_4(OClO_3)_2]ClO_4$	1107, 1046		621	328[a]	*36*
$[Fe(miqNO)_4(OClO_3)_2]ClO_4$	1117, 1095, 1047, 1020		637, 629, 621, 612	340[a], 330[a], 320[a]	*38*
$[Fe(mmpp)_2(H_2O)_2OClO_3]_2(ClO_4)_4$	1127, 1112, 1039	915	655, 640, 617	338[a]	*21*
$[Fe(phzNO_2)_3(H_2O)_2OClO_3](ClO_4)_2$	1123, 1068, 1038, 1021	926	652, 622, 617, 611	486	*41*
$[Fe(puHNO)_3(O_2ClO_2)](ClO_4)_2$	1133, 1095, 1077, 1050		648, 628, 619		*35*

[a] $\nu[M—O(ClO_4)]$.

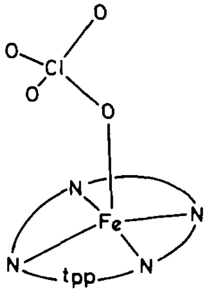


FIG. 3. Structure of Fe(tpp)$OClO_3$ complex. [Redrawn by permission from C. A. Reed *et al.*, *J. Am. Chem. Soc.* **101,** 2948 (1979).]

the tpp complex (2.029 Å) than in the oep complex (2.067 Å). Likewise, the coordinated O—Cl length (1.471 Å) in the former is shorter than that in the latter (1.515 Å). Further the coordinated O—Cl distances in both the complexes are appreciably longer than that of any of the uncoordinated ones (1.375, 1.406, and 1.408 Å for the tpp complex; 1.38, 1.41, and 1.45 Å for the oep complex). It is suggested that these results are consistent with considerable electron donation by the coordinated oxygen to the metal ion as well as $Fe \rightarrow (OCl)\pi^*$ back bonding. The Fe—O—Cl bond angles of 131.2 (tpp) and 125.7° (oep) indicate an sp^2 character for the oxygen bonding orbitals.

Reaction of ferrous and ferric perchlorates with pyzNO (L) in EtOH–teof yields complexes of the formulas $FeL_3(ClO_4)_2$ (red) and $FeL_6(ClO_4)_3$ (straw yellow), respectively (*48, 49*). The ferrous complex, on exposure to moisture, adds on a molecule of water, turning orange. The resulting aquo complex shows IR bands characteristic of coordinated perchlorate (Table III). A number of Fe(II) and Fe(III) complexes, containing donor molecules like mmpp, puHNO, phzNO, $phzNO_2$, quxNO, $quxNO_2$, and adH, have been proposed to involve unidentately or bidentately coordinated perchlorates (*21, 35, 39–41, 53*).

Christian and Roper (*57*) have isolated white crystals of a six-coordinate ruthenium(II) complex, *trans*-RuH(CO)(*p*-tNC)$(Ph_3P)_2OClO_3$ by treating the corresponding chloro complex with $AgClO_4$ in EtOH. The coordinated perchlorate can be readily displaced by CO or Ph_3P.

V. Complexes of Cobalt Group Metals

Peone and Vaska (*58, 59*) have reported the synthesis of a five-coordinate cobalt(I) complex, $Co(CO)_2(Ph_3P)_2OClO_3$, by treating the corresponding chloro complex with $AgClO_4$ in benzene. In a tetrahe-

TABLE IV

PERCHLORATE FREQUENCIES OF COBALT GROUP METAL COMPLEXES

Complex	Perchlorate bands (cm^{-1}) ν_3	ν_1	ν_4	Reference
$Co(CO)_2(Ph_3P)_2(OClO_3)$	1160, 1125, 1080	928	623	*58*
$Co(qun)_2(OClO_3)_2$	1105, 1095	920	634, 623, 463[a]	*47*
$[Co(mmpp)_4OClO_3]ClO_4$	1150, 1085, 1032	926	651, 637, 614, 312[b]	*21*
$[Co(tetp)_4OClO_3]ClO_4$	1141, 1105, 1050	920	650, 629, 619	*32*
$[Co(topo)_4OClO_3]ClO_4$	1149, 1119, 1085, 1029, 1011	977, 926	644, 621, 616, 467[a], 330[b]	*60*
$Co(Py)_4(OClO_3)_2$	1130, 1030	930	623, 615	*47*
$Co(4\text{-}MePy)_4(OClO_3)_2$	1137, 1020	925	625, 615	*47*
$Co(ad)(EtOH)(H_2O)_2OClO_3$	1120, 1085	920	640, 620	*53*
$[Co(bdpm)_2(O_2ClO_2)]ClO_4$	1185, 1100	985, 907	640, 623, 607	*51*
$[Co(NH_3)_5(OClO_3)](ClO_4)_2$	1190, 1115, 1035		658, 640, 620	*66*
$Rh(CO)(Ph_3P)_2(OClO_3)$	1160, 1130, 1070	920	620	*58*
$Ir(CO)(Ph_3P)_2(OClO_3)$	1160, 1130, 1050	920	620	*58*
$Ir(cod)(tfb)(OClO_3)$	1130, 1025		620	*69*

[a] ν_2.

[b] $\nu[M—O(ClO_4)]$.

dral cobalt(II) complex, $Co(qun)_2(ClO_4)_2$, the perchlorates are monodentately linked to the metal ion (*47*). A number of five-coordinate Co(II) complexes of the formulas $CoL_4(ClO_4)_2$ (L = Ph_2MeAsO, mmpp, tetp, topo; L_4 = tdaea) and $Co(adHNO)_2(EtOH)_2(ClO_4)_2$, in which one of the perchlorates is coordinated to the metal ion, have been characterized (Table IV) (*21, 23, 32–34, 46, 60*). $Co(Ph_2MeAsO)_4(ClO_4)_2$ is the first perchlorate complex whose crystal structure has been solved by X-ray analysis (*7*). It has a distorted tetragonal–pyramidal geometry (Fig. 4) wherein the apical position is occupied by one of the perchlorates with a Co—O distance of 2.10 Å and a Co—O—Cl angle of 130°.

A variety of six-coordinate cobalt(II) complexes of the compositions $Co(L—L)_2(ClO_4)_2$ (L—L = dth, bdpm, diars) (*8, 51, 61*), $CoL_3(H_2O)_2(ClO_4)_2 \cdot xH_2O$ (L = $phzNO_2$; $x = 4$; L = pyzNO; $x = 0$) (*41, 49*), $CoL_4(ClO_4)_2$ (L = β-PyBzl, Py, substituted pyridines; L_4 = bbtb) (*25, 47, 47a, 62*), and $CoL_5(ClO_4)_2$ (L = miqNO, NH_3, PhNC) (*38, 63, 64*) have been reported to contain coordinated perchlorate(s) (Table IV). The X-ray crystal structure analysis of $Co(dth)_2(ClO_4)_2$ complex (Fig. 5) shows monodentate coordination of both perchlorates at the apical positions with a Co—O bond length of 2.34 Å (*8*). The coordinated O—Cl length (1.47 Å) is longer than the uncoordinated ones (1.41 and

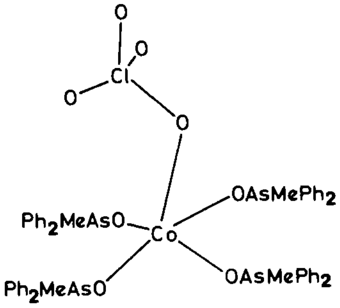


FIG. 4. Structure of $[Co(Ph_2MeAsO)_4OClO_3]^+$ complex ion. [Redrawn by permission from P. Pauling *et al.*, *Nature* (*London*) **207**, 73 (1965).]

1.43 Å). The diars complex has been isolated in two crystalline forms—monoclinic and orthorhombic. While the former has IR support for perchlorate coordination (*65*), the latter has X-ray crystal structure evidence (*61*) for very weak association of perchlorates with the metal ion in the axial positions. The PhNC complex exists in three isomeric forms, and the X-ray crystal structure of one of the forms (green), determined by Jurnak *et al.* (*64*), has indicated a perchlorate oxygen at the sixth coordination position around the metal ion with a Co—O distance of 2.594 Å and a Co—O—Cl angle of 135.6°. The coordinated O—Cl bond (1.396 Å) is longer than two of the uncoordinated ones (1.319, 1.327 Å) but is, however, shorter than the third one (1.413 Å). Karayannis and co-workers (*33, 34, 39, 40, 52, 53*) have characterized a series of perchlorate coordinated cobalt(II) complexes containing the ligands adHNO, phzNO, quxNO, quxNO$_2$, and adH (Table IV).

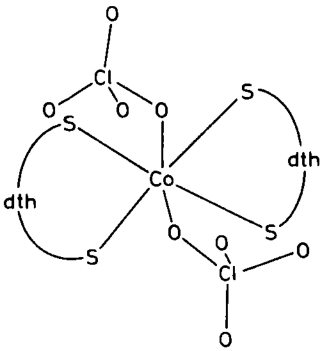


FIG. 5. Structure of $Co(dth)_2(OClO_4)_2$ complex. [Redrawn by permission from F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.* **87**, 4189 (1965).]

Harrofield *et al.* (*66*) have reported the isolation of a cobalt(III) complex, $[Co(NH_3)_5OClO_3](ClO_4)_2$, by treating $[Co(NH_3)_5N_3](ClO_4)_2$ with HNO_3–$NaNO_2$ in perchloric acid. Based on the changes in the visible spectra on addition of perchloric acid to the solutions of $[L_4Co\text{-}\mu\text{-}(NH_2, OH)CoL_4]^{4+}$ ($L = NH_3$; L_2 = en), formation of perchlorate complex cations of the type $[L_4Co\text{-}\mu\text{-}(NH_2, ClO_4)CoL_4]^{4+}$ has been envisaged (*67*).

Treatment of $MCl(CO)L_2$ (M = Rh, Ir; $L = Ph_3P$) complexes in benzene with $AgClO_4$ has yielded four-coordinate complexes of the type $M(CO)L_2(OClO_3)$ (*58, 59*). The perchlorate complexes undergo oxidative addition reactions with XY (H_2, HCl, Cl_2, organic halides, carboxylic acids, etc.) to produce six-coordinate complexes of the formula $M(CO)L_2(XY)OClO_3$ (*68*). In the parent complexes, the coordinated perchlorate is easily displaced by neutral molecules Q (C_2H_4, amines, Group V ligands, etc.) to produce cationic complexes of the composition $[M(CO)L_2Q]ClO_4$. $Ir(cod)(tfb)OClO_3$, isolated from the reaction mixture of $[IrCl(cod)]_2$, $AgClO_4$, and tfb in dichloromethane, also undergoes perchlorate substitution with Q (MeCN, $PhCH_2CN$) to yield $[Ir(cod)(tfb)Q]ClO_4$ (*69*). In complexes of type $M(CO)L_2A$ ($A = OClO_3$, anionic ligand) a relation between the carbonyl stretching frequency and the total electronegativity of A has been discerned (*70*). Accordingly, the total electronegativity of the perchlorate is found to be comparable to that of NCS^-.

VI. Complexes of Nickel Group Metals

Four-coordinate nickel(II) complexes of types $Ni(qun)_2(ClO_4)_2$ and $Ni(C_6Cl_5)L_2ClO_4$ ($L = PhMe_2P$, Ph_2MeP) involving monodentately coordinated perchlorates have been reported (*47, 71*). The latter ($L = PhMe_2P$) undergoes substitution of the perchlorate ligand with Q (CO, H_2O) to afford $[Ni(C_6Cl_5)L_2Q]ClO_4$. One of the two perchlorates is unidentately bound to the metal ion in several five-coordinate complexes of the formula $NiL_4(ClO_4)_2$ ($L = Me_3PO$, Ph_3PO, Me_3AsO, Ph_2MeAsO, Ph_3AsO, topo; L_4 = tdaea, tdpp, tdaa, dthp) (*23, 24, 26, 45, 46, 60, 72, 73*). While the topo complex is a 1 : 1 electrolyte in $MeNO_2$ (*60*), those containing the quadridentate ligands tdpp and tdaa show a similar behavior in $PhNO_2$ (*24*), supporting coordination of one of the perchlorates. The electronic spectral features of the latter complexes are characteristic of five-coordinate nickel(II). In the case of the dthp complex, the X-ray structure analysis shows perchlorate coordination with an Ni—O distance of 2.77 Å (*73*).

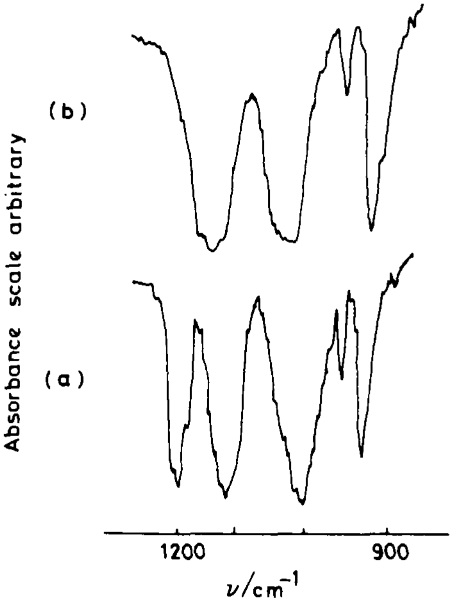


FIG. 6. IR spectra of (a) $Ni(MeCN)_2(ClO_4)_2$ and (b) $Ni(MeCN)_4(ClO_4)_2$ in the 1100 cm^{-1} region. [Reproduced by permission from A. E. Wickenden and R. A. Krause, *Inorg. Chem.* 4, 404 (1965).]

A variety of six-coordinate complexes of formulas $Ni(MeCN)_2(ClO_4)_2$ (*74*), Ni(L—L)$_2$(ClO$_4$)$_2$ (L—L = en, men, dmen, tmen, bada, bipy, phen, bdpm, dap, depNO, diars) (*51, 65, 75–79*), $NiL_4(ClO_4)_2$ (L = MeCN, Py, substituted pyridines, 2-*i*-PrIm, $PhNH_2$, aniline derivatives; L_4 = bbtb), and Ni(2-*i*-PrIm)$_4$XClO$_4$ (X = Cl, Br, I, SCN) (*22, 47, 62, 80–86*) involve coordination of perchlorate groups. Perchlorate frequencies of some of these complexes are listed in Table V. While monodentate coordination of both perchlorates has been shown in the men and dmen complexes by IR and electronic spectra and magnetic susceptibility measurements, bidentate coordination of both perchlorates has been postulated in $Ni(MeCN)_2(ClO_4)_2$ (Fig. 6) and Ni(tmen)$_2$(ClO$_4$)$_2$ complexes (*74, 75*). The solid-state reflectance spectrum of the latter complex indicates an octahedral environment for the metal ion and hence the following structure (Fig. 7a) has been suggested. However, an alternative structure (Fig. 7b) for the complex has been proposed, considering the fact that the tmen groups could also function as bidentate ligands. Aubry and Brown (*85*) have found a distorted octahedral structure for the 3,5-Me$_2$Py complex with monodentately linked per-

TABLE V

PERCHLORATE FREQUENCIES OF NICKEL GROUP METAL COMPLEXES

	Perchlorate bands (cm^{-1})			
Complex	ν_3	ν_1	ν_4	Reference
$Ni(C_6Cl_5)(Ph_2MeP)_2OClO_3$	1170, 1153, 1019			*71*
$Ni(qun)_2(OClO_3)_2$	1100, 1063	920	624, 616, 467[a]	*47*
$[Ni(Ph_3AsO)_4OClO_3]ClO_4$	1104, 1026		625, 614	*26*
$[Ni(topo)_4OClO_3]ClO_4$	1130, 1090, 1035	929	650, 621, 614, 466[a], 333[b]	*60*
$Ni(men)_2(OClO_3)_2$	1130, 1025	933	630, 616	*75*
$Ni(2\text{-}i\text{-}PrIm)_4(OClO_3)_2$	1110, 1055	930	620	*22*
$Ni(2\text{-}i\text{-}PrIm)_4Cl(OClO_3)$	1115, 1063	930	620	*22*
$Ni(en)_2(OClO_3)_2$	1130, 1093, 1058	962	638, 621	*77*
$Ni(depNO)_2(OClO_3)_2$	1075	918	628, 616, 439[a], 310[b]	*78*
$Ni(ad)(H_2O)_2(EtOH)OClO_3$	1125, 1089	921	638, 627	*53*
$Ni(PhNH_2)_4(OClO_3)_2$	1129, 1009	900	633, 613	*84*
$Ni(3,4\text{-}xylidine)_4(OClO_3)_2$	1139, 1034	928	638, 625	*84*
$[Ni(bdpm)_2(O_2ClO_2)]ClO_4$	1185, 1100	985, 907	640, 623, 607	*51*
$Ni(MeCN)_2(O_2ClO_2)_2$	1195, 1106, 1000	950, 920		*74*
$Ni(tmen)_2(O_2ClO_2)_2$	1170, 1125	928	635, 623, 617	*75*
$Pd(dppe)(OClO_3)_2$	1145, 1020	895	620, 610	*87*
$Pd(C_6F_5)(Ph_3As)_2OClO_3$	1150, 1015	870	630, 610	*88*
$Pt(C_6F_5)(Et_3P)_2OClO_3$	1170, 1020	870–850	650, 610	*92*

[a] ν_2.

[b] $\nu[M—O(ClO_4)]$.

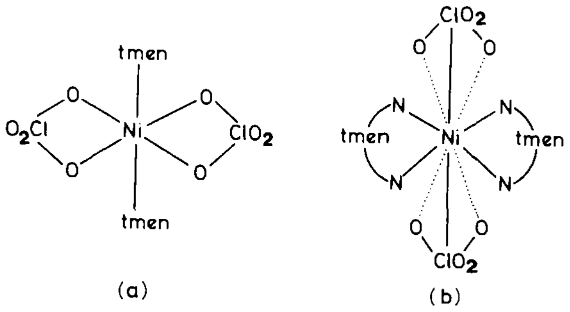


FIG. 7. Possible structures of $Ni(tmen)_2(ClO_4)_2$ complex. [Redrawn by permission from S. F. Pavkovic and D. W. Meek, *Inorg. Chem.* 4, 1091 (1965).]

chlorates having an Ni—O length of 2.187 Å and an Ni—O—Cl angle of 158°. The bonded O—Cl length is 1.40 Å as against the nonbonded ones, 1.24, 1.34, and 1.45 Å, the last one being anomalous. By contrast, the X-ray structure analysis of the 3,4-Me_2Py complex indicates the ionic nature of the perchlorates (*86*). Coordination of perchlorate has been identified in a number of six-coordinate nickel(II) complexes containing donor molecules like adHNO, miqNO, phzNO, $phzNO_2$, quxNO, $quxNO_2$, and adH (*33, 34, 38–41, 53*).

Unidentately bound perchlorates satisfy coordination number 4 for the metal ion in the $Pd(dppe)(ClO_4)_2$ complex, which is made by treating the corresponding dichloro complex with $AgClO_4$ in dichloromethane–benzene (*87*). The complex shows a very low molar conductance in dichloromethane, but behaves as a 1:2 electrolyte in such solvents as thf, MeCN, and MeOH, obviously owing to displacement of coordinated perchlorates by solvent molecules. Synthesis of $PdXL_2(OClO_3)$ ($X = C_6Cl_5$; $L = Ph_3P$; $X = C_6F_5$; $L = Et_3P$, $PhEt_2P$, Ph_2MeP, Ph_3P, Ph_3As; L_2 = dppe, bipy, phen, tamen) complexes has been accomplished by several workers (*88–90*). The coordinated perchlorate in such complexes is easily displaced by neutral molecules like 2-MePy, 3-MePy, 4-MePy, 2,4-Me_2Py and 3,5-Me_2Py to produce cationic complexes (*90*).

In $PtH(Ph_3P)_2ClO_4$, the perchlorate is presumably coordinated, but supporting evidence is not available (*91*). Monodentate coordination of perchlorate has been visualized in the case of $Pt(C_6F_5)(Et_3P)_2ClO_4$ (*92*). Since the complex has a perchlorate band at 1170 cm^{-1} (Table V), it is likely that ClO_4^- is bidentate. The complex is a 1:1 electrolyte in Me_2CO and $MeNO_2$. Substitution of the coordinated perchlorate with a variety of donor groups readily takes place to produce

TABLE VI

PERCHLORATE FREQUENCIES OF COPPER GROUP METAL COMPLEXES

Complex	Perchlorate bands (cm^{-1})			Reference
	ν_3	ν_1	ν_4	
$Cu(Cy_3P)_2OClO_3$	1120, 1020	910	618, 610	*95*
$Cu(Cy_3As)_2OClO_3$	1110, 1100, 1022	906	625, 620	*94*
$Cu(triphos)OClO_3$	1130, 1025	905	615, 610	*95*
$Cu(Ph_3P)_3OClO_3$	1130, 1050	930		*97*
$[Cu(Ph_3P)_2(O_2ClO_2)]_2$	1165, 1140, 1035	920		*97*
$Cu(Ph_2EtAs)_3OClO_3$	1122, 1077, 1033	911	616, 613	*94*
$Cu(Ph_2\text{-}n\text{-}PrAs)_3OClO_3$	1117, 1078, 1033	916	619, 614	*94*
$[Cu(quxNO_2)_4OClO_3]ClO_4$	1134, 1093, 1065, 1050	932	649, 623, 618, 454[a]	*40*
$Cu(NH_3)_4(OClO_3)_2$	1105, 1050	914		*110*
$Cu(Py)_4(OClO_3)_2$	1107, 1040	929	625, 619	*47*
$Cu(en)_2(OClO_3)_2$	1130, 1050	927	624, 464[a]	*118b*
$Cu(1\text{-}ViIm)_4(OClO_3)_2$	1130, 1045	932	625	*112*
$Cu(dmpNO)_2(OClO_3)_2$	1143, 1090	941	639, 631	*122*
$[Cu(dpa)(MeCO_2)(O_2ClO_2)]ClO_4$	1145, 1110, 1070	935, 930	637, 630, 625, 460[a]	*106*
$Cu(qun)_2(O_2ClO_2)_2$	1100, 1050	930	633, 620	*47*
$Cu(arg)_2(O_2ClO_2)_2$	1140, 1115, 1085		635, 630, 625	*127*
$Ag(Cy_3P)OClO_3$	1150, 1000	850		*131*
$Ag(Cy_3As)_2(OClO_3)$	1105, 1083, 1040	910	623, 616	*94*
$Ag(Nap_2EtAs)_2(OClO_3)$	1117, 1112, 1035	915	626, 622	*94*
$Ag(Ph_2EtAs)_3(OClO_3)$	1104, 1075, 1040	920	620, 614	*94*
$Ag(Iotz)_2(O_2ClO_2)$	1140, 1095, 1050	930		*132*

[a] ν_2.

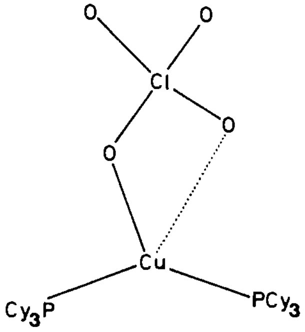


FIG. 8. The geometry about the copper atom in $Cu(Cy_3P)_2ClO_4$. [Reproduced by permission from R. J. Restivo *et al.*, *Can. J. Chem.* **53**, 1949 (1975).]

$[Pt(C_6F_5)(Et_3P)_2Q]ClO_4$ (Q = H_2O, Pr_2NH, Py, CO, Et_3P, Ph_3P, Ph_3As, Ph_3PO, Ph_3PS) complexes. On the basis of molar conductance and UV spectral results, it is presumed that the complex $Pt_2(pdpa)_2(NCS)_2(ClO_4)_2$ contains one monodentate perchlorate (*92a*).

VII. Complexes of Copper Group Metals

Among the perchlorate ion complexes of metals, those of copper have been widely studied, especially their X-ray crystal structure analyses. Copper(II) perchlorate reacts with bulky ligands in an ethanol medium to produce colorless copper(I) complexes of the composition CuL_2ClO_4 (L = Cy_3P, Cy_3As) (*93, 94*). The complexes have monodentately bound perchlorate as indicated by their IR spectra (Table VI), but they behave as 1:1 electrolyes in $PhNO_2$. Ferguson and co-workers (*95*) have confirmed the coordination of perchlorate to the metal ion in the Cy_3P complex by X-ray crystal structure analysis. The perchlorate is found to be unidentate but disordered over two sites (Fig. 8), with a bonded Cu—O length of 2.22 Å and a nonbonded intramolecular contact Cu ··· O of 3.203 Å. The coordinated O—Cl distance (1.46 Å) is close to the average (1.43 Å) of the uncoordinated ones (1.38, 1.41, and 1.50 Å). The coordination geometry around the metal ion is distorted trigonal. In another complex, $Cu(triphos)ClO_4$, containing a tridentate phosphine, it has been envisaged that the metal ion is either three- or four-coordinate involving monodentate perchlorate.

A few four-coordinate complexes of the formulas CuL_3ClO_4 (L = Ph_3P, Ph_2EtAs, Ph_2-*n*-PrAs; L_3 = tox) and $Cu(Ph_3P)_2ClO_4$ have been reported (*94, 96, 97*); the last one is a dimer with bridging bidentate

TABLE VII

BOND LENGTHS AND BOND ANGLES OF COPPER PERCHLORATE COMPLEXES

		Bond length (Å)		Bond angle (°)	
Complex	Coordination kernel	Cu—O	O—Cl	Cu—O—Cl	Reference
$Cu(Cy_3P)_2(OClO_3)$	CuP_2O	2.22	1.46	122.4	*95*
$Cu(tox)_3(OClO_3)$	CuS_3O	2.278	1.478	126.9	*96*
$[Cu(bpdt)OClO_3]ClO_4$	CuS_2N_2O	2.264	1.448	—	*99*
$\{[Cu(tmdt)OClO_3]_2Imz\}ClO_4$	CuN_4O	2.412	1.39	132.6	*101*
		2.379	1.41	133.6	
$[Cu(eaep)(OH)OClO_3]_2$	CuN_2O_3	2.562	1.391	139.8	*102*
		2.618	1.406	130.7	
$[Cu(dmaep)(OH)OClO_3]_2$ (β)	CuN_2O_3	2.721	1.422	123.0	*103*
$[Cu(dmaep)(OH)O_2ClO_2]_2$ (α)	CuN_2O_4	2.716	1.429	117.7	*10*
		2.782	1.437	121.2	
$[Cu(2\text{-}MeIm)_2(OH)(O_2ClO_2)]_2 \cdot 2H_2O$	CuN_2O_4	2.827			*104*
$Cu(dpa)(MeCO_2)(O_2ClO_2) \cdot H_2O$	CuN_2O_4	2.541	1.396		*106*
		2.638	1.387		
$Cu(pam)_2(OClO_3)_2$	CuN_2O_4	2.52	1.38	143.1	*120*
$[Cu(bipy)_2(O_2ClO_2)]ClO_4$	CuN_4O_2	2.73	1.48	124	*9*
		2.45	1.48		
		2.746	1.438		*105*
		2.512	1.418		

$Cu(Im)_4(OClO_3)_2$	CuN_4O_2	2.625			*111*
$Cu(aep)_2(OClO_3)_2$	CuN_4O_2	2.833	1.433	148.8	*6*
$Cu(en)_2(OClO_3)_2$	CuN_4O_2	2.611	1.414	122.6	*108*
$Cu(dab)_2(OClO_3)_2$					
(blue-violet)	CuN_4O_2	2.579	1.451	126.2	*116*
(red-violet)	CuN_4O_2	2.676	1.387	125.1	
$Cu(dap)_2(OClO_3)_2$	CuN_4O_2	2.61	1.45	120	*116a*
$Cu(men)_2(OClO_3)_2$	CuN_4O_2	2.575	1.431	121.0	*118*
$Cu(pyz)_2(OClO_3)_2$	CuN_4O_2	2.373	1.426	170.6	*119*
$Cu(dmpd)_2(OClO_3)_2$	CuN_4O_2	2.602	1.441	123.7	*121*
$Cu(hism)_2(OClO_3)_2$	CuN_4O_2	2.616	1.422		*123*
$Cu(bpda)(OClO_3)_2$	CuN_4O_2	2.693	1.438	142.1	*5*
$Cu(tamn)(OClO_3)_2$	CuN_4O_2	2.667	1.454	118.9	*113*
		2.527	1.448	121.1	
$Cu(Im)_2(Gly—GlyH)OClO_3$	CuN_3O_3	2.97			*128*
$Cu(mmea)_2(OClO_3)_2$	$CuN_2S_2O_2$	2.599	1.447	130.1	*124*
$Cu(pmmi)_2(OClO_3)_2$	$CuN_2S_2O_2$	2.594	1.436	139.3	*126*
$Cu(dth)_2(OClO_3)_2$	CuS_4O_2	2.549	1.446		*117*
$Cu(tctd)(OClO_3)_2$	CuS_4O_2	2.652	1.441	130.3	*114*
$Cu(ompa)_2(OClO_3)_2$	CuO_6	2.546	1.407	149.5	*125*
$[Cu(Imzn)_5(OClO_3)]ClO_4$	CuO_6	2.994			*109*

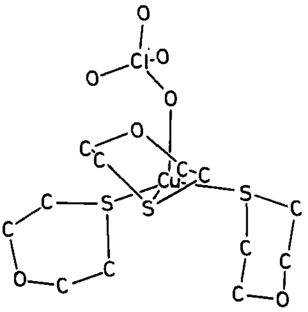


FIG. 9. A perspective drawing of $Cu(tox)_3OClO_3$. [Reproduced by permission from M. M. Olmstead *et al.*, *Transition Met. Chem.* **7**, 140 (1982).]

perchlorates. The X-ray crystal structure analysis of the tox complex (*96*) shows trigonal–pyramidal geometry around copper(I) with strongly coordinated unidentate perchlorate (Fig. 9; Table VII). The bonded O—Cl length (1.478 Å) is longer than the nonbonded ones (1.40, 1.413, and 1.42 Å).

Four-coordination involving one monodentate perchlorate in each case has been visualized for the metal ion in copper(II) complexes of the compositions $Cu(bpes)(ClO_4)_2$ (*98*) and $Cu(phzNO_2)_3(ClO_4)_2 \cdot H_2O$ (*41*). A variety of five-coordinate complexes of the formulas $Cu(bpdt)(ClO_4)_2$ (*99*), $Cu(deta)XClO_4$ (X = Cl, Br, OAc, etc.) (*100*), $Cu_2(tmdt)_2(\mu\text{-Imz})(ClO_4)_3$ (*101*), $[Cu(N—N)(\mu\text{-OH})ClO_4]_2$ (N—N = eaep, dmaep) (*102, 103*), $Cu(quxNO)_2(H_2O)_2(ClO_4)_2 \cdot H_2O$, $Cu(quxNO_2)_3(ClO_4)_2 \cdot 10H_2O$, and $CuL_4(ClO_4)_2$ (L = miqNO, $quxNO_2$; L_4 = tdaea) (*23, 38–40*), containing coordinated perchlorate, have been reported. The X-ray crystal structure of the bpdt complex, solved by Brubaker *et al.* (*99*), indicates that the metal ion assumes a square–pyramidal configuration with two nitrogen and two sulfur atoms of the tetradentate ligand occupying the basal plane and a perchlorate oxygen the apex. Similarly, pentacoordination for each of the metal ions in the binuclear tmdt complex is satisfied by four nitrogen atoms (three from the tridentate tmdt ligand and one from the bridging Imz ion) and a monodentate perchlorate (*101*). Hodgson and co-workers (*102, 103*) have described the geometry around the metal ion in each of the dimeric complexes containing eaep (violet) and dmaep (dark blue, monoclinic, β-form) as two adjoining distorted tetragonal pyramids with a common edge defined by the two bridging hydroxyl oxygen atoms. Thus the basal plane at each copper consists of two nitrogens of the bidentate ligand (Fig. 10; N—N = eaep or dmaep) and two bridging oxygens (of OH groups)

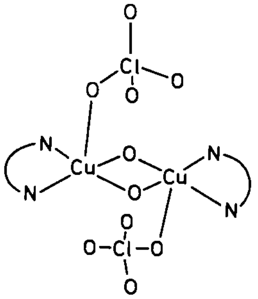


FIG. 10. Structure of $[Cu(N—N)(OH)ClO_4]_2$. [Redrawn by permission from D. L. Lewis *et al.*, *Inorg. Chem.* **13,** 1013 (1974).]

while the fifth coordination site is occupied by a perchlorate oxygen. The metal–perchlorate interaction has been proposed to be weak.

The α isomer (deep blue, triclinic) of the dmaep complex is also dinuclear but six-coordinate. The IR spectrum of this form shows very intense peaks at 1145, 1128, and 1072 cm^{-1}, which have been assigned to bidentate perchlorate. This deduction has been confirmed by crystallographic evidence (*10*). The perchlorates are positioned directly above and below the planar central dimeric $[(dmaep)Cu(\mu\text{-}OH)_2Cu(dmaep)]^{2+}$ unit (Fig. 11), each linked to the two copper atoms via two

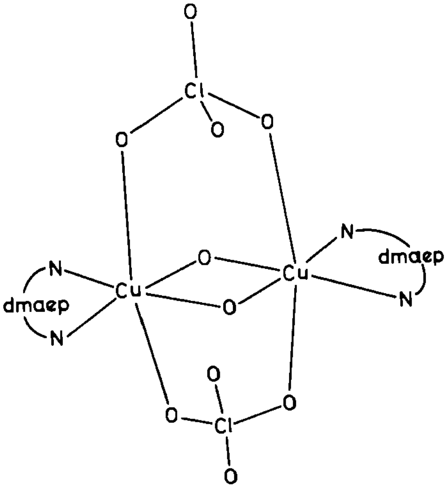


FIG. 11. Structure of α-$[Cu(dmaep)(OH)ClO_4]_2$. [Redrawn by permission from D. L. Lewis *et al.*, *Inorg. Chem.* **13,** 147 (1974).]

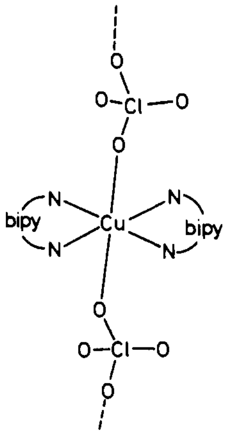


FIG. 12. Structure of a part of the infinite chain, $[\mathrm{Cu(bipy)_2ClO_4^+}]_\infty$. [Redrawn by permission from H. Nakai, *Bull. Chem. Soc. Jpn.* **44**, 2412 (1971).]

oxygens. Further, one of the two remaining oxygen atoms of each perchlorate is hydrogen bonded to the bridging hydroxyl hydrogen with OH ··· O contact of 2.36 Å. The coordinated O—Cl distances (Table VII) are longer than the uncoordinated ones, 1.409 and 1.428 Å. Intramolecular bidentate coordination of perchlorates has also been confirmed in another dihydroxo-bridged complex of the formula $[\mathrm{Cu(2\text{-}MeIm)_2(OH)ClO_4}]_2 \cdot 2H_2O$ by X-ray structure analysis (*104*). The distorted octahedral coordination around each metal ion is completed by two nitrogen atoms of 2-MeIm.

Nakai (*9*) has recognized an intermolecular bidentate perchlorate of a polymeric nature in $\mathrm{Cu(bipy)_2(ClO_4)_2}$, based on X-ray photographic data collection. The coordination polyhedron around the copper atom is a tetragonally distorted octahedron (Fig. 12) wherein the four N atoms of bipy molecules are arranged in a flattened tetrahedral manner, the least-squares plane of these atoms making an equatorial plane, while the axial positions are occupied by the oxygen atoms of perchlorates. However, there is coexistence of coordinated and noncoordinated perchlorates in the crystal. Hathaway and co-workers (*105*) have redetermined the bond-length parameters more accurately in the above complex, using X-ray diffractometer data collection (Table VII). The crystal structure of $\mathrm{Cu(dpa)(MeCO_2)ClO_4 \cdot H_2O}$, solved by the above workers (*106*), has also indicated a polymeric nature with an elongated rhombic octahedral geometry for the complex in which the axial positions are occupied by oxygen atoms from the unsymmetrically bridging perchlorate groups. X-ray structure analysis of the

$Cu(en)_2(ClO_4)_2$ complex by Pajunen (*107, 108*) has shown unidentate coordination of both perchlorates in the long tetragonal positions above and below the planar $[Cu(en)_2]^{2+}$ unit.

A wide range of other six-coordinate complexes of copper(II) of the types $Cu(Imzn)_5(ClO_4)_2$ (*109*), $CuL_4(ClO_4)_2$ (L = MeCN, NH_3, Py, 4-MePy, Im, 1-ViIm, 1-Vi-2-MeIm, 2-EtIm, 2-*i*-PrIm; L_4 = bpda, bbtb, tamn, tctd) (*5, 15, 47, 47a, 62, 110–115*), $Cu(L—L)_2(ClO_4)_2$ (L—L = en, aep, dab, dap, dth, men, pyz, pam, bdpm, dmpd, dmpNO, hism, mmea, ompa, pmmi) (*1, 6, 51, 116–126*), $CuL_2(ClO_4)_2$ (L = qun, arg) (*47, 127*), $Cu(Im)_2(Gly—GlyH)ClO_4$ (*128*), and $Cu(tbma)XClO_4$ (X = Cl, Br) (*27*), involving coordinated perchlorates, have been reported. The X-ray studies on the blue crystals of the Imzn complex, carried out by Majeste and Trepons (*109*), have shown that one of the perchlorates completes the distorted octahedral stereochemistry for the metal ion. The Cu—O distance of 2.994 Å found for this complex appears to be the longest bond length observed among copper perchlorate complexes (Table VII). According to crystal structure analysis by Ivarsson (*111*), the perchlorates in the Im complex have been located at the apical positions of an octahedron around the metal ion. On the basis of IR data (Table VI), the monodentate nature of perchlorates has been envisaged in the complexes containing Py, 4-MePy, and substituted Im (*47, 112*). As indicated by X-ray crystal structure studies, the complexes involving the tetradentate ligands bpda (*5*), tamn (*113*), and tctd (*114*) have a tetragonal coordination for the metal ion with unidentate perchlorates at the axial sites. Likewise, the perchlorates in $Cu(L—L)_2(ClO_4)_2$ complexes are shown to occupy elongated trans positions of an octahedron. In this series, the structure of the pyrazine complex has been found to be made up of parallel sheets each having an infinite square array of the metal ions bridged by the nonchelating bidentate pyz molecules (Fig. 13). Each metal ion, with a tetragonally elongated octahedral environment, is linked strongly to four nitrogen atoms of four pyz groups and weakly to two monodentate perchlorates. The large Cu—O—Cl angle lying in the range 160–170° is thought to minimize nonbonded interactions between ClO_4^- ions, which are linked to the metal ions on adjacent sheets (*119*). A weak coordination of perchlorates has been visualized in the complex having the chelating bidentate ligand pam (*120*). The coordinated O—Cl length, 1.38 Å, in the latter complex is surprisingly shorter than the average (1.41 Å) of the uncoordinated ones (1.31, 1.43, and 1.50 Å). However the metal ion bound O—Cl distance (1.441 Å) in the dmpd complex (Fig. 14) is longer than the nonbonded ones (1.401, 1.418, and 1.429 Å) (*121*). For this complex, the effect of temperature on the IR bands of the perchlorate

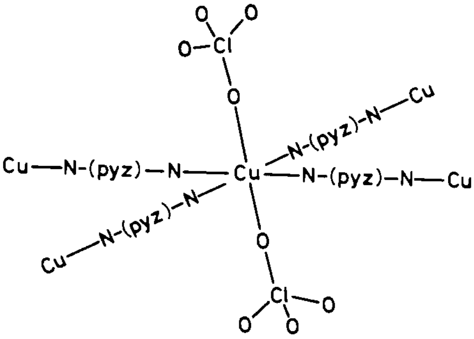


FIG. 13. A section of the sheet structure in $Cu(pyz)_2(ClO_4)_2$. [Redrawn by permission from J. Darriet *et al.*, *Inorg. Chem.* **18**, 2679 (1979).]

has been studied. As seen in Fig. 15, the splitting of the ν_3 band decreases with increasing temperature.

Electronic and IR spectra and other physical techniques are in consonance with a distorted octahedral structure for $CuL_2(ClO_4)_2$ (L = qun, arg) complexes, implying that the perchlorates are bidentate (*47, 127*). Bell *et al.* (*128*) have worked out the crystal structure of a distorted octahedral complex, $Cu(Im)_2(Gly—GlyH)ClO_4$, containing a dipeptide; the perchlorate occupies an apical position. Infrared spectra have revealed monodentate coordination of perchlorates in copper(II) complexes having ligands such as adH, adHNO, pyzNO, quxNO, and an octadentate Schiff base (*33, 34, 39, 49, 52, 53, 129*).

The structure of a trinuclear complex, $Cu_3(Im)_8(Imz)_2(ClO_4)_4$ (*130*), has been described to consist of three octahedrally (distorted) coordi-

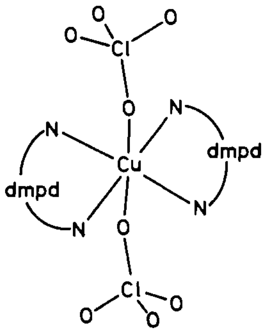


FIG. 14. Structure of $Cu(dmpd)_2(ClO_4)_2$. [Redrawn by permission from L. P. Battaglia *et al.*, *J. Chem. Soc. Dalton Trans.* 8 (1981).]

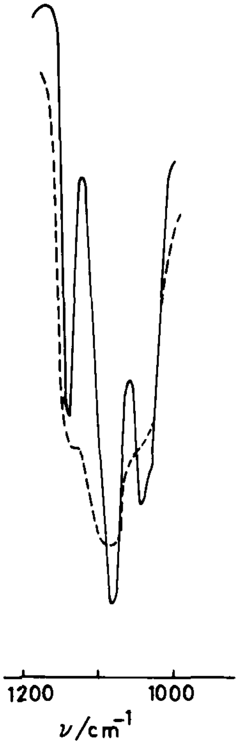


FIG. 15. IR spectra of $Cu(dmpd)_2(ClO_4)_2$ at 293 (——) and 393 K (---) in the 1200–950 cm^{-1} region. [Reproduced by permission from L. P. Battaglia *et al.*, *J. Chem. Soc. Dalton Trans.* 8 (1981).]

nated copper atoms, one of them connected through two Imz bridges to the other two (Fig. 16). Thus the centrosymmetric metal atom (Cu-1) is attached to four N atoms (two from each of the Im and Imz groups) and two O atoms of bridging perchlorates, while each of the two symmetry-related metal atoms (Cu-2) are also linked to four N atoms (three from Im and one from Imz ligands) and two O atoms of terminal and bridging perchlorates. Consequently, there are two types of perchlorates—one is bidentate, bridging to both Cu-1 and Cu-2 with Cu—O distances 2.755 and 2.93 Å, respectively, and the other is unidentately bound to Cu-2 with Cu—O length 2.581 Å. The reason for the difference between the first two values has been ascribed to the fact that the 2.755 Å refers to the Cu-1 octahedron having both perchlorates as bidentate bridging, while 2.93 Å refers to the Cu-2 octahedron with two different perchlorates, one shared and the other unshared.

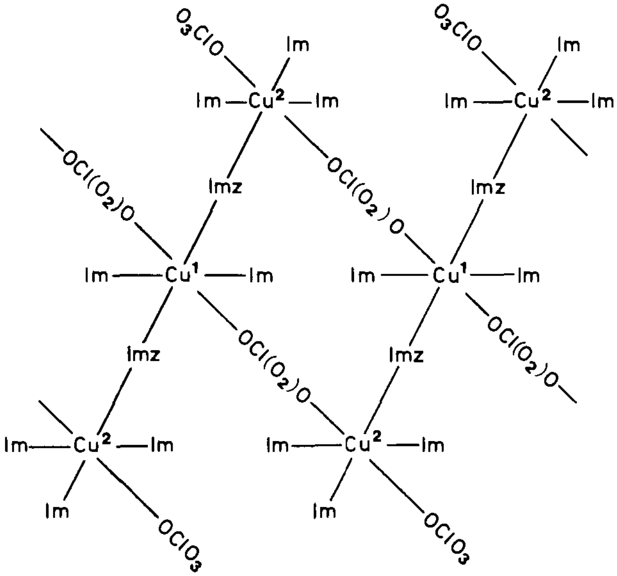


FIG. 16. Structure of $Cu_3(Im)_8(Imz)_2(ClO_4)_4$. [Redrawn by permission from G. Ivarsson *et al.*, *Acta Chem. Scand.* **26**, 3005 (1972).]

A number of two-coordinate silver(I) complexes of the type $AgLOClO_3$ (L = *t*-Bu_3P, Cy_3P, *o*-$tolyl_3P$, (*p*-$XC_6H_4)_3P$ (X = F, Cl, OMe) have been prepared by Dikhoff and Goel (*131*). The complexes are stable in the solid state and are unionized in dichloromethane. Naikar *et al.* (*94*) have obtained three- and four-coordinate complexes (Table VI) of the formulas $AgL_2(OClO_3)$ (L = Nap_2EtAs, Cy_3As) and $AgL_3(OClO_3)$ (L = Ph_2EtAs, Ph_2-*n*-PrAs) by treating $AgClO_4$ with tertiary arsines in alcohol. Stoichiometric quantities of $AgClO_4$ and Iotz in aqueous medium has yielded four-coordinate $Ag(Iotz)_2(O_2ClO_2)$ complex (*132*). $AgClO_4$ reacts with tmb in MeOH–MeCN to give colorless crystals of $Ag_2(tmb)_3(ClO_4)_2$. According to X-ray diffraction studies, the complex has infinite chains wherein each metal ion is bonded to three CN groups of tmb ligands and weakly to an oxygen atom of perchlorate. Thus the metal ion has a trigonal–pyramidal geometry with Ag—O 2.733, O—Cl (bonded) 1.416 Å, and Ag—O—Cl angle 129.2° (*133*). The structure of another complex, $Ag(dmso)_2ClO_4$, is also shown by X-ray studies to be built up of infinite chains of metal ions joined by double bridging dmso oxygen atoms. For this complex, a distorted trigonal–bipyramidal geometry around each metal ion with a chelating bidentate perchlorate (Ag—O = 2.411, 2.741 Å) has been described (*134*).

Syntheses of perchlorate-coordinated gold(I) and gold(III) complexes of the types, $AuLClO_4$, $Au_2(dppm)(ClO_4)_2$, and $Au(C_6F_5)_2LClO_4$ (L = Ph_3P) have been described by Uson and co-workers (*135–137*). The coordinated perchlorate can easily be displaced by cod in the former Ph_3P complex (135) and by anionic (N_3^-, HCO_3^-) or neutral monodentate (Et_3P, Bu_3P, Ph_2MeP, Ph_3PO, Ph_3AsO, PyNO, etc.) ligands in the latter (*138*).

VIII. Complexes of Zinc Group Metals

Reaction of zinc(II) perchlorate with tertiary arsines in thf–teof yields complexes of compositions $Zn(Cy_3As)_2(ClO_4)_2$ and $ZnL_3(ClO_4)_2$ (L = Ph_2MeAs, Ph_2EtAs) (*94*). Unidentate coordination of one of the perchlorates to the metal ion in each of the above complexes has been inferred from the solid-state IR spectra (Table VIII). In the case of the Cy_3As complex, perchlorate coordination continues to exist in dichloromethane solution (*139*). A planar three-coordinate structure for the Cy_3As complex and a tetrahedral configuration for the other two complexes in the solid state have been visualized. Tetrahedral complexes of stoichiometries $Zn(qun)_2(OClO_3)_2$ (*47*) and $Zn(miqNO)_3(OClO_3)ClO_4 \cdot H_2O$ (*38*) have also been characterized.

Several zinc(II) complexes of the formulas $ZnL_4(ClO_4)_2$ (L = mmpp, tetp, Ph_2MeAsO; L_4 = taea) (*21, 32, 46, 140*), $Zn(adHNO)_2(H_2O)_2(ClO_4)_2$ (*34*), $Zn_2(phzNO)_4(H_2O)_2(ClO_4)_4 \cdot 6H_2O$ (*39*), and Zn(Tpp)-ClO_4 (*13*), where the metal ion is five-coordinate, have been reported. Infrared evidence has been presented for monodentate coordination of one of the perchlorates to the metal ion in each of these complexes. Perchlorate coordination to the metal ion persists in dichloromethane, as shown by the IR spectrum of the Tpp complex. Spaulding *et al.* (*13*) have elucidated the structure of the above complex by the X-ray diffraction method. The complex has unidentate perchlorate at the apex of a square pyramid (Fig. 17) with a Zn—O distance of 2.07 Å and a Zn—O—Cl angle of 130.2°. The metal-bound O—Cl length is 1.451 Å, as against the nonbonded ones of 1.328, 1.374, and 1.525 Å. In the phzNO complex, the metal ions are bridged through two molecules of the *N*-oxides (*39*). Six-coordinate zinc(II) complexes of the types $Zn(MeCN)_4(ClO_4)_2$ (*15*), $Zn(pyzNO)_4(ClO_4)_2 \cdot H_2O$ (*49*), $Zn(phzNO_2)_3(ClO_4)_2 \cdot 5H_2O$ (*41*), $Zn(bdpm)_2(ClO_4)_2$ (*51*), and $Zn_2L_6(ClO_4)_4 \cdot xH_2O$ (L = quxNO, $x = 10$; L = $quxNO_2$, $x = 12$) (*39, 40*) are considered to involve one or two monodentate perchlorates. In the dimeric complexes, the metal ions are again bridged by two of the *N*-oxide ligands.

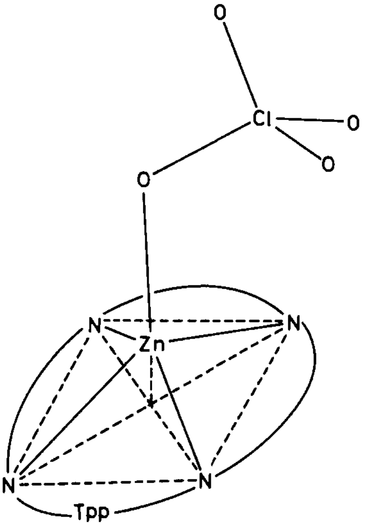


FIG. 17. Geometry about the zinc atom in Zn(Tpp)$OClO_3$. [Reproduced by permission from L. D. Spaulding *et al.*, *J. Am. Chem. Soc.* **96**, 982 (1974).]

Perchlorate coordination has been identified in only a few complexes in the case of cadmium. Cadmium(II) perchlorate reacts with tertiary arsines in thf–teof to afford $Cd(Cy_3As)_2(ClO_4)_2$ and $Cd(Ph_2RAs)_3(ClO_4)_2$ (R = Me, Et, *n*-Pr) complexes (*94*). It has been envisaged on the basis of IR data (Table VIII) that one of the perchlorates is serving as a monodentate ligand. As a consequence, a planar three-coordinate structure for the Cy_3As complex and a tetrahedral configuration for the rest of the complexes have been proposed. $Cd(bdpm)_2(ClO_4)_2$ is suggested to involve a bidentate perchlorate (*51*) and hence coordination number 6 for the metal ion. A variable coordination number (6 or 7) for the metal ion is postulated in the $CdL(ClO_4)_2$ (L = pentagonal Schiff base) complex (*129*).

A series of mercury(II) complexes of stoichiometries $HgL_2(ClO_4)_2$ (L = Cy_3P, *t*-Bu_3P, *o*-$tolyl_3P$, $mesityl_3P$, Cy_3As, Nap_2MeAs, Nap_2EtAs), $Hg(Ph_2EtAs)_2(H_2O)(ClO_4)_2$, and $HgL_3(ClO_4)_2$ (L = Ph_3P, *p*-$tolyl_3P$, Ph_2MeAs, Ph_2EtAs, Ph_2-*n*-PrAs) have been prepared by treating mercuric perchlorate with tertiary phosphines or arsines in alcohol (*141, 142*). Coordination of one or two perchlorates in each of these complexes is indicated by the IR spectra (Table VIII). Thus the metal ion is thought to have planar three-coordination in $HgL_2(ClO_4)_2$ (L = tertiary arsine) complexes, and a tetrahedral geometry in the other series. However, $HgL_2(ClO_4)_2$ complexes containing tertiary phosphines

TABLE VIII

PERCHLORATE FREQUENCIES OF ZINC GROUP METAL COMPLEXES

Complex	Perchlorate bands (cm^{-1})			Reference
	ν_3	ν_1	ν_4	
$[Zn(Cy_3As)_2OClO_3]ClO_4$	1127, 1100, 1044	927	625, 620	*94*
$[Zn(Ph_2MeAs)_3OClO_3]ClO_4$	1128, 1110, 1084, 1047	920	622, 612	*94*
$[Zn(miqNO)_3OClO_3]ClO_4 \cdot 3H_2O$	1110, 1090, 1053, 1015		641, 626, 619, 612, 328[a]	*38*
$Zn(qun)_2(OClO_3)_2$	1107, 1085	925	635, 624, 483[b]	*47*
$[Zn(taea)OClO_3]ClO_4$	1147, 1094, 1001	930	654, 621	*140*
$[Zn(mmpp)_4OClO_3]ClO_4$	1141, 1085, 1040	927	652, 647, 616, 310[a]	*21*
$[Zn(tetp)_4OClO_3]ClO_4$	1140, 1095, 1048	924	647, 631, 622	*32*
$[Zn(pyzNO)_4(H_2O)OClO_3]ClO_4$	1115, 1097, 1081		621, 293[a]	*49*
$[Cd(Cy_3As)_2OClO_3]ClO_4$	1122, 1105, 1082, 1050	930	624, 619	*94*
$[Cd(Ph_2MeAs)_3OClO_3]ClO_4$	1127, 1089, 1079, 1033	911	623, 620	*94*
$[Cd(Ph_2EtAs)_3OClO_3]ClO_4$	1130, 1085, 1038	928	624, 622	*94*
$[Cd(Ph_2\text{-}n\text{-}PrAs)_3OClO_3]ClO_4$	1135, 1105, 1082, 1050	910	623, 613	*94*
$[Hg(Cy_3As)_2OClO_3]ClO_4$	1130, 1115, 1080, 1040	915	625, 621, 618	*142*
$[Hg(Nap_2MeAs)_2OClO_3]ClO_4$	1135, 1115, 1090, 1025	910	623, 618, 615	*142*
$Hg(Ph_3P)_2(OClO_3)_2$	1190, 1022	912	618, 612	*144*
$[Hg(Ph_3P)_3OClO_3]ClO_4$	1130, 1085, 1025	910	623, 614	*142*
$[Hg(p\text{-}tolyl_3P)_3OClO_3]ClO_4$	1125, 1090, 1030	920	620, 615	*142*
$[Hg(Ph_2EtAs)_2(H_2O)OClO_3]ClO_4$	1120, 1115, 1085, 1030	915	628, 625, 620	*142*
$[HgCl(o\text{-}tolyl_3P)OClO_3]_2$	1110, 1070, 1045	925, 917	686, 666, 622	*145*
$[Hg(Ph_3P)OClO_3(O_2ClO_2)]_2$	1120, 1080, 1020	906, 896	620, 616, 580	*144*

[a] $\nu[M—O(ClO_4)]$.

[b] ν_2.

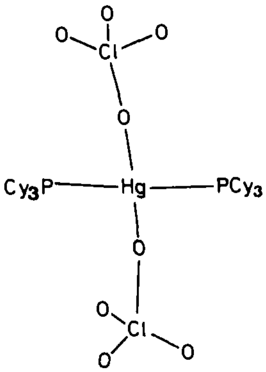


FIG. 18. Structure of $Hg(Cy_3P)_2(OClO_3)_2$ molecule. [Redrawn by permission from E. C. Aleya *et al.*, *J. Chem. Res. Synop.* 360 (1979).]

are considered to be four-coordinate (*141*). Although the Cy_3P complex had earlier been characterized as a two-coordinate species on the basis of IR spectra and ^{31}P and ^{199}Hg chemical shift results (*143*), X-ray diffraction analysis has indicated weak coordination of perchlorates to the metal ion (Fig. 18) with Hg—O distances of 2.928 and 3.234 Å (*141*); however, the latter value appears to be too large for a covalent bond length. Tetrahedral complexes of the types $HgL_2(OClO_3)_2$ and $[HgL(OClO_3)(O_2ClO_2)]_2$ (L = Ph_3P, Ph_3As) have been reported by Davis *et al.* (*144*).

In an attempt to isolate a 1:2 complex from the reaction mixture of mercuric perchlorate and *o*-tolyl$_3$P, Aleya *et al.* (*145*) have obtained a dichloro-bridged dinuclear complex [HgCl(*o*-tolyl$_3$P)ClO_4]$_2$. The complex is a nonelectrolyte in dichloromethane, and the monodentate nature of the perchlorate is shown by the IR spectrum as well as by X-ray crystallographic analysis. The coordination geometry around each of the metal ions is described as trigonal–bipyramidal with an equatorial site unoccupied (Fig. 19). The weakly bound perchlorate is situated at one of the equatorial positions with Hg—O 2.73, O—Cl (coordinated) 1.42, and O—Cl (terminal) 1.36, 1.41, and 1.44 Å.

Sandström (*146*) has established by X-ray analysis unidentate coordination of two of the perchlorates to one of the metal ions (Hg—O length = 2.78, 3.04 Å; Hg—O—Cl angle = 161, 123°) in the binuclear complex $Hg_2(dmso)_8(ClO_4)_4$. The metal ions bridged through two of the eight dmso molecules assume distorted octahedral geometries. X-ray evidence has been presented by Epstein *et al.* (*147*) for the presence of a weakly bonded perchlorate in a seven-coordinate mercury(II) complex

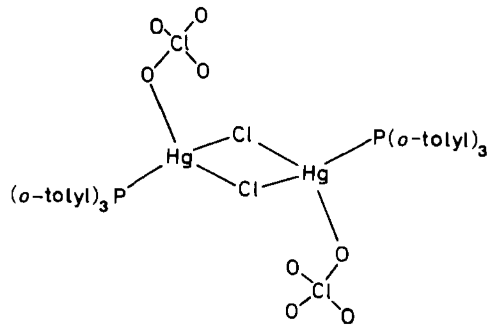


FIG. 19. Structure of $[HgCl(o\text{-tolyl}_3P)OClO_3]_2$. [Redrawn by permission from E. C. Aleya *et al.*, *Can. J. Chem.* **57**, 2217 (1979).]

$Hg(ntd)_3(ClO_4)_2$ with Hg—O length = 2.93; O—Cl length = 1.34 (bonded), 1.28, 1.34, and 1.35 Å (nonbonded), and Hg—O—Cl angle = 114°. In another Hg(II) complex, $Hg(tchd)(ClO_4)_2$, having a tetradentate macrocyclic tetrathioether ligand, the metal ion is visualized as having heptacoordination, though its morphology is that of an irregular, tetragonally elongated octahedron. The metal ion in the complex has been located by X-ray diffraction studies near the center of the four S atoms of the macrocycle, and the inner coordination sphere is completed by both perchlorates, which are unequally bonded along the z axis, one being monodentate (Hg—O, 2.76 Å) and the other being weakly bidentate (Hg—O, 3.08 and 3.26 Å) (*148*).

IX. Complexes of Lanthanides

On treatment of lanthanide perchlorates with Q in MeOH–teof, six-coordinate complexes of the type $LnQ_4(ClO_4)_3$ (Ln = Ce; Q = n-Bu_3PO, Ph_3PO; Ln = Nd; Q = ttp), in which two of the perchlorates are covalently linked to the metal ion, are obtained (*18, 20, 36*). The cerium complex is a 1 : 1 electrolyte in $MeNO_2$, implying that the two ClO_4^- groups continue to be coordinated in solution. On the basis of analytical results and IR and conductance measurements, several lanthanide complexes containing hmpa have been formulated as $[Ln(hmpa)_4(OClO_3)_2]ClO_4$ (Ln = La, Nd, Gd, Ho, Yb), indicating hexacoordination for the metal ion. However, detailed IR and Raman spectral studies indicate bidentate coordination of one or more of the perchlorates, suggesting that the coordination number of the lanthanide ion may vary from six to eight in these systems (*17, 29*). $CeQ_6(ClO_4)_3$ (Q = tmp, dmmp) and Nd(phen)$_3$(ClO$_4$)$_3$ complexes are postulated to involve a monodentate perchlorate (*28, 149–151*). Seven-coordination for the metal ion in these complexes is assigned, based on the facts that the former is a 1:2 electrolyte in MeNO$_2$, while the latter shows strong IR peaks at 1100 (split) and 927 cm^{-1}. Unidentate coordination of two of the perchlorates in Ln(CypNO)$_n$(ClO$_4$)$_3$ · 2H$_2$O (n = 5; Ln = Gd, Tb; n = 6; Ln = La, Sm, Dy, Ho; n = 7; Ln = Pr, Nd, Er, Yb) complexes is revealed by IR and molar conductivity measurements (*151a*).

The IR spectra of Ln(III) complexes Ln(tdod)(ClO$_4$)$_3$ · xH$_2$O (Ln = Ce, Pr, x = 1; Ln = Nd, x = 0) are consistent with the presence of exclusively unidentate perchlorates (*31*). The complexes are 1:2 electrolytes in MeCN, and thus one of the perchlorates continues to be attached to the metal ion in solution. Lanthanide ions also form a number of other 10-coordinate complexes having coordinated perchlorates, namely, LnQ(ClO$_4$)$_3$ · S (Ln = Sm, Eu, Yb; Q = htod; S = H$_2$O; Ln = Eu; Q = dtod; S = H$_2$O; Ln = Pr, Nd, Eu; Q = hdhc; S = MeCN; Ln = Ce, Pr, Nd, Sm, Eu, Dy, Ho; Q = tdhc) (*11, 31, 152*). Ciampolini *et al.* (*11, 152*) have elucidated the structures of Sm(tdhc)(ClO$_4$)$_3$ and Eu(hdhc)(ClO$_4$)$_3$ by X-ray diffraction. The coordination polyhedron around the metal ion is a hexagonal bipyramid (having six oxygens of the tdhc ligand in the equatorial plane and four oxygens of the perchlorates at the apices) for the former, and a square bicapped antiprism (with two nitrogen atoms in axial positions and eight oxygen atoms at the vertices of the two squares) for the latter. Thus all three perchlorates are linked to the samarium ion, one of them being bidentate (Sm—O length = 2.64, O—Cl length = 1.46 Å, Sm—O—Cl angle = 101.2°) while the other two are monodentate (Sm—O length = 2.36, O—Cl length = 1.48 Å, Sm—O—Cl angle = 152.5°). On the other hand, only one of the perchlorates is bidentately bound to the europium ion (Eu—O lengths = 2.67, 2.71; O—Cl lengths = 1.47, 1.62 Å). A coordination geometry similar to that around the samarium ion is ascribed to the other Ln(tdhc)(ClO$_4$)$_3$ complexes. These are 1:2 electrolytes in MeCN at low concentrations (10^{-3} *M*), but behave as 1:1 electrolytes in slightly more concentrated solutions (10^{-2} *M*).

Bidentate coordination of one or two perchlorates has been proposed in a thorium(IV) complex of composition Th(Ph$_3$PO)$_4$(ClO$_4$)$_4$ (*20*).

X. Complexes of Other Metals

The crystal structure studies on Na(ebsmCu)$_2$ClO$_4$ by Milburn *et al.* (*153*) have indicated an octahedral environment for the sodium ion, with the perchlorate serving as a chelating bidentate ligand (Na—O =

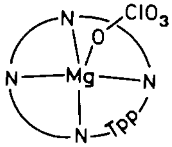


FIG. 20. Structure of Mg(Tpp)$OClO_3$. [Redrawn by permission from K. M. Barkigia *et al.*, *Inorg. Chem.* **22,** 349 (1983).]

2.60 Å). Barkigia *et al.* (*154*) have deduced the crystal structure of Mg(Tpp)ClO_4, wherein the metal ion has a square–pyramidal geometry, with one of the oxygens of the perchlorate at the apex (Fig. 20). The Mg—O length (2.012 Å) appears to be the shortest among the M—O distances known for metal perchlorato complexes; the Mg—O—Cl angle = 134.5°. The preparation of a calcium(II) complex $[Ca(Ph_3PO)_4(O_2ClO_2)]ClO_4$ {$\nu(ClO_4)$ 1190, 1144, 1025, 935, 656, 625, 611, 490, and 460; $\nu[Ca—O(ClO_4)]$ 318 cm^{-1}} has been reported (*20*). In $Al(tetp)_4(ClO_4)_3$, unidentate coordination of two of the perchlorates has been suggested, based on its molar conductance in $MeNO_2$ and the occurrence of perchlorate bands at 1120, 1090, 1042, 920, 652, 638, and 621 cm^{-1} in the IR spectrum (*32*). Matyashin *et al.* (*155*) have briefly mentioned the preparation of compounds of type $R_4N(MX_3ClO_4)$ (R = Me, Et, Bu; M = B, Al; X = F, Cl, Br, BH_4) having coordinated perchlorate. An indium(III) complex of the formula $[In(Ph_3PO)_4(OClO_3)_2]ClO_4$ [$\nu(ClO_4)$ 1140, 1030, 920, 650, 627, 609, 480, and 455; $\nu(In—OClO_3)$ 311 cm^{-1}] is known (*20*). Blundell and Powell (*156*) have elucidated the crystal structure of a thallium(III) complex $TlMe_2(phen)ClO_4$ wherein the six-coordinate metal ion is surrounded by a pentagonal–bipyramidal environment with an equatorial position vacant. The weakly bonded perchlorate behaves as a bidentate-bridging ligand between two metal ions with a Tl—O length of 2.88 Å.

X-Ray crystal structure analysis of the dianion $(SnCl_3ClO_4)^{2-}$ reveals a square–pyramidal geometry around the metal ion (*157*). The equatorial plane is defined by two Cl atoms, one perchlorate oxygen, and presumably the unshared electron pair of tin. The perchlorate is monodentate (Sn—O length = 2.907, coordinated O—Cl length = 1.426 Å, Sn—O—Cl angle = 135.9°), and the coordinated O—Cl distance is longer than the uncoordinated ones (1.392, 1.399, and 1.410 Å). A trigonal–bipyramidal configuration and hence pentacoordination for the metal ion in $SnMe_3ClO_4$ is satisfied by bidentate-bridging perchlorate (*158*). In another tin complex, $[Sn_3O_2Cl_4(ClO_4)_4]_2$, the X-ray diffraction, IR, and Raman spectral investigations are consistent with the occurrence of strongly bonded two unidentate and six biden-

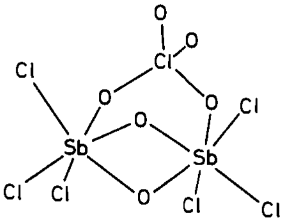


FIG. 21. Structure of $Sb_2Cl_6O(OH)(O_2ClO_2)$ molecule. [Redrawn by permission from C. H. Belin *et al.*, *Inorg. Chem.* **21**, 3557 (1982).]

tate bridging perchlorates with an average Sn—O distance of 2.16 Å (*159*).

The covalent nature of perchlorate is envisaged in several antimony complexes of formulas $(SbMe_3ClO_4)_2O$, $(SbPh_3ClO_4)_2O$, $(SbPh_3ClO_4)_2O \cdot 2H_2O$, $Sb_2Cl_6O(OH)ClO_4$, and $Sb_8Cl_{24}O_5(ClO_4)_6$ (*14, 160, 161*). The perchlorates in $(SbMe_3ClO_4)_2O$ are shown to be unidentate (Sb—O length = 2.60, O—Cl length = 1.443 Å, Sb—O—Cl angle = 134.7°), and the metal ions are five-coordinate with trigonal–bipyramidal geometry (*161*). X-Ray diffraction and IR and Raman spectra of $Sb_2Cl_6O(OH)ClO_4$ provide evidence for bidentate-bridging perchlorate (Fig. 21) with Sb—O distances of 2.207 and 2.247 Å; each antimony atom has a distorted octahedral environment. The bridging O—Cl lengths of 1.477 and 1.479 Å are appreciably longer than the terminal ones (1.390 and 1.398 Å) (*14*). Perchlorate coordination is also observed in a few bismuth complexes of the types $(BiPh_3ClO_4)_2O$ and $(BiPh_3ClO_4)_2O \cdot 2H_2O$ (*160, 161*). March and Ferguson (*162*) have carried out X-ray diffraction of the former, and a distorted trigonal–bipyramidal environment around each of the bismuth atoms (bridged through an oxygen atom) with equatorial phenyls was found (Fig. 22). In contrast to the case of $(SbMe_3ClO_4)_2O$, while only one of the perchlorates is monodentate, having Bi—O length = 2.655, O—Cl length = 1.48 Å, Bi—O—Cl angle = 132.5°, the other is disordered between two sites with Bi—O lengths = 2.53, 2.76; O—Cl lengths = 1.46, 1.36 Å; Bi—O—Cl angles = 137.5, 126.7°.

XI. Conclusion

It is evident that a majority of the metals form perchlorato complexes provided care is taken to eliminate from the system water and other anions, especially halides. The O—Cl bond of the M—O—Cl unit

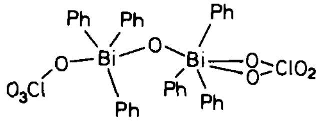


FIG. 22. Structure of $(BiPh_3ClO_4)_2O$. [Redrawn by permission from F. C. March and G. Ferguson, *J. Chem. Soc. Dalton Trans.* 1291 (1975).]

is generally longer than the uncoordinated ones of ClO_4^-, though there are a few exceptions. Coordination of perchlorate and the resulting change in the stereochemical environment around the metal ion is manifest where possible in the magnetic and electronic spectral properties of the metal complex. Similarly, the lowering of the symmetry of ClO_4^- owing to coordination is amply reflected in the IR and Raman spectral features. For several complexes, ν(M—O) is found around 330 cm^{-1}, implying considerable covalent character in the metal–perchlorate bond. It is likely that appreciable M→O backbonding exists in some of the complexes. Nevertheless, the M—O bond is usually weak, and the term "semicoordination" aptly describes the situation.

The coordinated oxygen atom may be visualized as having sp^2 hybridization, and the observed M—O—Cl bond angle is expected to reflect the M—O bond strength. In practice this may not be true since steric factors involving other ligands play a dominant role in perchlorate coordination. Attempts to evaluate the M—O bond strength in perchlorato complexes would be quite interesting.

Stable as well as transitory perchlorate-coordinated species are convenient intermediates for the isolation of novel complexes. With four potential donor sites, the role of ClO_4^- acting as a bridging ligand perhaps has interesting possibilities yet to be revealed.

XII. Abbreviations

aep, 2-[-2-(Aminoethyl)]pyridine
adH, Adenine
adHNO, Adenine *N*(1)-oxide
arg, Arginine

bada, Biacetyldianil
bbtb, *p,p'*-Bis(benzoylthiourea)-biphenyl
bdpm, Bis(3,5-dimethylpyrazolyl)methane
bipy, 2,2'-Bipyridine
bpda, 1,8-Bis-(2'-pyridyl)-3,6-diazaoctane
bpdt, 1,8-Bis-(2'-pyridyl)-3,6-dithiaoctane
bpes, Bis-[β-pyridyl-(2)-ethyl] sulfide

Bu, Butyl
Bzl, Benzimidazole

cod, Cycloocta-1,5-diene
Cy, Cyclohexyl
CypNO, 4-Cyanopyridine *N*-oxide

dab, 1,3-Diaminobutane
dap, 1,2- or 1,3-Diaminopropane
depf, Diethylphosphonoformate anion
depNO, 2-Diethylaminopyridine *N*-oxide
deta, Diethylenetriamine
diars, *o*-Phenylenebisdimethylarsine
dmaep, 2-(2-Dimethylaminoethyl)pyridine
dmen, *N,N'*-Dimethylethylenediamine
dmf, *N,N'*-Dimethylformamide
dmmp, Dimethyl methylphosphonate
dmp, 2,2'-Dimethoxypropane
dmpd, 2,2-Dimethylpropane-1,3-diamine
dmpNO, 2-Dimethylaminopyridine *N*-oxide
dmso, Dimethyl sulfoxide
dpa, Di-2-pyridylamine
dpNO, 2,6-Dimethylpyridine *N*-oxide
dppe, 1,2-Bis(diphenylphosphino)ethane
dppm, 1,1-Bis(diphenylphosphino)methane
dth, 2,5-Dithiahexane
dthp, 2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene
dtod, 1,10-Dioxa-4,7,13,16-tetrathiacyclooctadecane

eaep, 2-(2-Ethylaminoethyl)pyridine
ebsm, *N,N'*-Ethylenebis(salicyleneiminato)
en, Ethylenediamine
ESR, Electron spin resonance
Et, Ethyl

Gly–GlyH, Glycylglycine anion

hdhc, 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
hism, Histamine
hmpa, Hexamethylphosphoramide
htod, 1,4,7,10,13,16-Hexathiacyclooctadecane

Im, Imidazole
Imz, Imidazolate anion
Imzn, 2-Imidazoline
Iotz, 2-Imino-4-oxa-1,3-thiazolidine
IR, Infrared

M, Metal ion
Me, Methyl
men, *N*-Methylethylenediamine
miqNO, 3-Methylisoquinoline *N*-oxide
mmea, β-Methylmercaptoethylamine
mmpp, Methyl methylphenylphosphinate

Nap, Naphthyl
ntd, 1,8-Naphthyridine

oep, Octaethylporphinato dianion
ompa, Octamethylphosphoramide

pam, Pyridine-2-acetamide
Ph, Phenyl
phen, 1,10-Phenanthroline
phzNO, Phenazine *N*-oxide
phzNO$_2$,Phenazine *N*,*N*-dioxide
pmmi, 4-(*n*-Propylmercaptomethyl)imidazole
Pr, Propyl
puHNO, Purine *N*(1)-oxide
Py, Pyridine
β-PyBzl, β-Pyridylbenzimidazole
pyz, Pyrazine
pyzNO, Pyrazine *N*-oxide

qun, Quinoline
quxNO, Quinoxaline *N*-oxide
quxNO$_2$, Quinoxaline 1,4-dioxide

taea, Tris(2-aminoethyl)amine
tamen, *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine
tamn, 2,3,2-Tetraamine
tbma, Tris(2-benzimidazolylmethyl)amine
tchd, 1,5,9,13-Tetrathiacyclohexadecane
tctd, 1,4,8,11-Tetrathiacyclotetradecane
tdaa, Tris(*o*-diphenylarsinophenyl)arsine
tdaea, Tris(2-dimethylaminoethyl)amine
tdhc, 5,6,14,15-Tetrahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin
tdod, 1,4,10,13-Tetraoxa-7,16-dithiacyclooctadecane
tdpp, Tris(*o*-diphenylphosphinophenyl)phosphine
teof, Triethyl orthoformate
tetp, Triethyl thiophosphate
tfb, Tetrafluorobenzobarrelene
thf, Tetrahydrofuran
tmb, 2,5-Dimethyl-2,5-diisocyanohexane
tmdt, 1,1,7,7-Tetramethyldiethylenetriamine
tmen, *N*,*N*,*N'*-Trimethylethylenediamine
tmp, Trimethyl phosphate

p-tNC, *p*-Tolyl isocyanide
topo, Tri-*n*-octylphosphine oxide
tox, 1,4-Thioxane
tpp, *meso*-Tetraphenylporphinate dianion
Tpp, Tetraphenylporphinate anion
triphos, 1,1,1-Tris(diphenylphosphinomethyl)ethane
ttp, Tri-*p*-tolyl phosphate

UV, Ultraviolet
Vi, Vinyl

REFERENCES

1. Brown, D. S., Lee, J. D., Melsom, B. G. A., Hathaway, B. J., Procter, I. M., and Tomlinson, A. A. G., *J. Chem. Soc. Chem. Commun.* 369 (1967).
2. Rosenthal, M. R., *J. Chem. Educ.* **50,** 331 (1973).
3. Johansson, L., *Coord. Chem. Rev.* **12,** 241 (1974).
4. Davies, J. A., and Hartley, F. R., *Chem. Rev.* **81,** 79 (1981).
5. Wright, D. A., and Quinn, J. D., *Acta Crystallogr. Sect. B* **30,** 2132 (1974).
6. Lewis, D. L., and Hodgson, D. J., *Inorg. Chem.* **13,** 143 (1974).
7. Pauling, P., Robertson, G. B., and Rodley, G. A., *Nature (London)* **207,** 73 (1965).
8. Cotton, F. A., and Weaver, D. L., *J. Am. Chem. Soc.* **87,** 4189 (1965).
9. Nakai, H., *Bull. Chem. Soc. Jpn.* **44,** 2412 (1971).
10. Lewis, D. L., Hatfield, W. E., and Hodgson, D. J., *Inorg. Chem.* **13,** 147 (1974).
11. Ciampolini, M., Nardi, N., Cini, R., Mangani, S., and Orioli, P., *J. Chem. Soc. Dalton Trans.* 1983 (1979).
12. Reed, C. A., Mashiko, T., Bentley, S. P., Castner, M. E., Scheidt, W. R., Spartalian, K., and Long, G., *J. Am. Chem. Soc.* **101,** 2948 (1979).
13. Spaulding, L. D., Eller, P. G., Bertrand, J. A., and Felton, R. H., *J. Am. Chem. Soc.* **96,** 982 (1974).
14. Belin, C. H., Chaabouni, M., Pascal, J. L., and Potier, J., *Inorg. Chem.* **21,** 3557 (1982).
15. Hathaway, B. J., and Underhill, A. E., *J. Chem. Soc.* 3091 (1961).
15a. Hathaway, B. J., *Curr. Contents* (45), 20 (1982).
16. Ross, S. D., *Spectrochim. Acta* **18,** 225 (1962).
16a. Pearson, G. S., *Adv. Inorg. Radiochem.* **8,** 190 (1966).
17. Scholer, R. P., and Merbach, A. E., *Inorg. Chim. Acta* **15,** 15 (1975).
18. Karayannis, N. M., Mikulski, C. M., Pytlewski, L. L., and Labes, M. M., *Inorg. Chem.* **9,** 582 (1970).
19. Karayannis, N. M., Mikulski, C. M., Pytlewski, L. L., and Labes, M. M., *Inorg. Chim. Acta* **10,** 97 (1974).
20. Karayannis, N. M., Mikulski, C. M., Strocko, M. J., Pytlewski, L. L., and Labes, M. M., *J. Inorg. Nucl. Chem.* **32,** 2629 (1970).
21. Mikulski, C. M., Unruh, J., Pytlewski, L. L., and Karayannis, N. M., *Transition Met. Chem.* **4,** 98 (1979).
22. Pujari, P., and Dash, K. C., *J. Inorg. Nucl. Chem.* **38,** 1891 (1976).
23. Ciampolini, M., and Nardi, N., *Inorg. Chem.* **5,** 41 (1966).
24. Dyer, G., Hartley, J. G., and Venanzi, L. M., *J. Chem. Soc.* 1293 (1965).

25. Shashikala, N., Leelamani, E. G., and Reddy, G. K. N., *Indian J. Chem.* **21A,** 743 (1982).

26. Goodgame, D. M. L., Goodgame, M., and Hayward, P. J., *J. Chem. Soc. A* 1352 (1970).

27. Addison, A. W., Hendriks, H. M. J., Reedijk, J., and Thompson, L. K., *Inorg. Chem.* **20,** 103 (1981).

28. Graham, P., and Joesten, M., *J. Inorg. Nucl. Chem.* **32,** 531 (1970).

29. Durney, M. T., and Marianelli, R. S., *Inorg. Nucl. Chem. Lett.* **6,** 895 (1970).

30. Crawford, N. P., and Melson, G. A., *J. Chem. Soc.* 141 (1970).

31. Ciampolini, M., Mealli, C., and Nardi, N., *J. Chem. Soc. Dalton Trans.* 376 (1980).

32. Mikulski, C. M., Chauhan, S., Rabin, R., and Karayannis, N. M., *J. Inorg. Nucl. Chem.* **43,** 2017 (1981).

33. Mikulski, C. M., Iaconianni, F. J., Pytlewski, L. L., Speca, A. N., and Karayannis, N. M., *Inorg. Chim. Acta* **46,** L47 (1980).

34. Mikulski, C. M., de Prince, R., Tran, T. B., Iaconianni, F. J., Pytlewski, L. L., Speca, A. N., and Karayannis, N. M., *Inorg. Chim. Acta* **56,** 163 (1981).

35. Mikulski, C. M., de Prince, R., Tran, T. B., and Karayannis, N. M., *Inorg. Chim. Acta* **56,** 27 (1981).

36. Mikulski, C. M., Pytlewski, L. L., and Karayannis, N. M., *Inorg. Chim. Acta* **32,** 263 (1979).

37. Mikulski, C. M., Marks, B., Tuttle, D., and Karayannis, N. M., *Inorg. Chim. Acta* **68,** 119 (1983).

38. Speca, A. N., Gelfand, L. S., Iaconianni, F. J., Pytlewski, L. L., Mikulski, C. M., and Karayannis, N. M., *Inorg. Chim. Acta* **33,** 195 (1979).

39. Karayannis, N. M., Speca, A. N., Chasan, D. E., and Pytlewski, L. L., *Coord. Chem. Rev.* **20,** 37 (1976).

40. Chasan, D. E., Pytlewski, L. L., Owens, C., and Karayannis, N. M., *J. Inorg. Nucl. Chem.* **40,** 1019 (1978).

41. Chasan, D. E., Pytlewski, L. L., Owens, C., and Karayannis, N. M., *J. Inorg. Nucl. Chem.* **41,** 13 (1979).

42. Jones, K. M., and Bjerrum, J., *Acta Chem. Scand.* **19,** 974 (1965).

43. Wimmer, F. L., and Snow, M. R., *Aust. J. Chem.* **31,** 267 (1978).

44. Snow, M. R., and Wimmer, F. L., *Inorg. Chim. Acta* **44,** L189 (1980).

45. Brodie, A. M., Hunter, S. H., Rodley, G. A., and Wilkins, C. J., *Inorg. Chim. Acta* **2,** 195 (1968).

46. Lewis, J., Nyholm, R. S., and Rodley, G. A., *Nature (London)* **207,** 72 (1965).

47. Brown, D. H., Nuttal, R. H., McAvoy, J., and Sharp, D. W. A., *J. Chem. Soc.* 892 (1966).

47a. Jones, W. C., and Bull, W. E., *J. Chem. Soc. A* 1849 (1968).

48. Speca, A. N., Pytlewski, L. L., and Karayannis, N. M., *Inorg. Nucl. Chem. Lett.* **9,** 365 (1973).

49. Speca, A. N., Karayannis, N. M., and Pytlewski, L. L., *J. Inorg. Nucl. Chem.* **35,** 3113 (1973).

50. Karayannis, N. M., Mikulski, C. M., Strocko, M. J., Pytlewski, L. L., and Labes, M. M., *J. Inorg. Nucl. Chem.* **33,** 3185 (1971).

51. Reedijk, J., and Verbiest, J., *Transition Met. Chem.* **4,** 239 (1979).

52. Speca, A. N., Gelfand, L. S., Iaconianni, F. J., Pytlewski, L. L., Mikulski, C. M., and Karayannis, N. M., *Inorg. Chim. Acta* **37,** L 551 (1979).

53. Speca, A. N., Gelfand, L. S., Iaconianni, F. J., Pytlewski, L. L., Mikulski, C. M., and Karayannis, N. M., *J. Inorg. Nucl. Chem.* **43,** 2771 (1981).

54. Horn, E., and Snow, M. R., *Aust. J. Chem.* **33,** 2369 (1980).

55. Phillips, D. J., and Tyree, S. Y., *J. Am. Chem. Soc.* **83,** 1806 (1961).

56. Masuda, H., Taga, T., Osaki, K., Sugimoto, H., Yosida, Z. I., and Ogoshi, H., *Inorg. Chem.* **19,** 950 (1980).

57. Christian, D. F., and Roper, W. R., *J. Chem. Soc. Chem. Commun.* 1271 (1971).

58. Peone, J., Jr., and Vaska, L., *Angew. Chem. Int. Ed.* **10,** 511 (1971).

59. Peone, J., Jr., Flynn, B. R., and Vaska, L., *Inorg. Synth.* **15,** 68 (1974).

60. Mikulski, C. M., Pytlewski, L. L., and Karayannis, N. M., *Synth. Inorg. Met. Org. Chem.* **9,** 401 (1979).

61. Einstein, F. W. B., and Rodley, G. A., *J. Inorg. Nucl. Chem.* **29,** 347 (1967).

62. Satpathy, K. C., Mishra, H. P., and Patel, B. N., *Indian J. Chem.* **22A,** 338 (1983).

63. Dual, R., *Ann. Chim.* **18,** 259 (1932).

64. Jurnak, F. A., Greig, D. R., and Raymond, K. N., *Inorg. Chem.* **14,** 2585 (1975).

65. Rodley, G. A., and Smith, P. W., *J. Chem. Soc. A* 1580 (1967).

66. Harrowfield, J. M., Sargeson, A. M., Singh, B., and Sullivan, J. C., *Inorg. Chem.* **14,** 2864 (1975).

67. Tayer, R. S., and Sykes, A. G., *J. Chem. Soc. Chem. Commun.* 1137 (1969).

68. Vaska, L., and Peone, J., Jr., *Suom. Kemistil. B* **44,** 317 (1971).

69. Uson, R., Oro, L. A., Carmona, D., and Esteruelas, M. A., *Inorg. Chim. Acta* **73,** 275 (1983).

70. Vaska, L., and Peone, J., Jr., *J. Chem. Soc. Chem. Commun.* 418 (1971).

71. Wada, M., and Oguro, M., *Inorg. Chem.* **15,** 2346 (1976).

72. Cotton, F. A., and Bannister, E., *J. Chem. Soc.* 1873 (1960).

73. Dewar, R., and Fleischer, E., *Nature (London)* **222,** 372 (1969).

74. Wickenden, A. E., and Krause, R. A., *Inorg. Chem.* **4,** 404 (1965).

75. Pavkovic, S. F., and Meek, D. W., *Inorg. Chem.* **4,** 1091 (1965).

76. Harris, C. M., and McKenzie, E. D., *J. Inorg. Nucl. Chem.* **29,** 1047 (1967); *J. Inorg. Nucl. Chem.* **19,** 372 (1961).

76a. Barker, N. T., Harris, C. M., and McKenzie, E. D., *Proc. Chem. Soc.* 335 (1961).

77. Farago, M. E., James, J. M., and Trew, V. C. G., *J. Chem. Soc. A* 820 (1967).

78. West, D. X., and O'Grady, T. J., *J. Inorg. Nucl. Chem.* **43,** 2725 (1981).

79. Pajunen, A., *Suom. Kemistil. B* **42,** 397 (1969); *Chem. Abstr.* **71,** 129682u (1969).

80. Moore, L. E., Gayhart, R. B., and Bull, W. E., *J. Inorg. Nucl. Chem.* **26,** 896 (1964).

81. Bull, W. E., and Moore, L. E., *J. Inorg. Nucl. Chem.* **27,** 1341 (1965).

82. Buffagni, S., Vallarino, L. M., and Quagliano, J. V., *Inorg. Chem.* **3,** 671 (1964).

83. Vallarino, L. M., Hill, W. E., and Quagliano, J. V., *Inorg. Chem.* **4,** 1598 (1965).

84. Butcher, A. V., Phillips, D. J., and Redfern, J. P., *J. Chem. Soc. A* 1064 (1968).

85. Aubry, F. M., and Brown, G. M., *Acta Crystallogr. Sect. B* **24,** 745 (1968).

86. Aubry, F. M., Busing, W. R., and Brown, G. M., *Acta Crystallogr. Sect. B* **24,** 754 (1968).

87. Davies, J. A., Hartley, F. R., and Murray, S. G., *J. Chem. Soc. Dalton Trans.* 2246 (1980).

88. Uson, R., Fornies, J., and Gonzalo, S., *J. Organomet. Chem.* **104,** 253 (1976).

89. Uson, R., Royo, P., and Fornies, J., *Synth. Inorg. Met. Org. Chem.* **4,** 157 (1974).

89a. Uson, R., Fornies, J., and Martine, F., *J. Organomet. Chem.* **112,** 105 (1976).

90. Coronas, J. M., Polo, C., and Sales, J., *Synth. Inorg. Met. Org. Chem.* **10,** 53 (1980).

91. Gavrilova, I. V., Gel'fnan, M. I., Ivannikova, N. V., and Razumovskii, V. V., *Russ. J. Inorg. Chem.* **16,** 596 (1971).

92. Uson, R., Royo, P., and Gimeno, J., *J. Organomet. Chem.* **72,** 299 (1974).

92a. Sandhu, S. S., Chavla, S., and Parmar, S. S., *Transition Met. Chem.* **6,** 246 (1981).

93. Moers, F. G., and Op Het Veld, P. H., *J. Inorg. Nucl. Chem.* **22,** 3225 (1970).
94. Naikar, S. B., Nanje Gowda, N. M., and Reddy, G. K. N., *Indian J. Chem.* **23A,** 133 (1984).
95. Restivo, R. J., Costin, A., Ferguson, G., and Carty, A. J., *Can. J. Chem.* **53,** 1949 (1975).
96. Olmstead, M. M., Musker, W. K., and Kessler, R. M., *Transition Met. Chem.* **7,** 140 (1982).
97. Cariati, F., and Naldini, L., *J. Inorg. Nucl. Chem.* **28,** 2243 (1966); *Gazz. Chim. Ital.* **95,** 3 (1965).
98. Uhlig, E., and Heinrich, G., *Z. Anorg. Allg. Chem.* **330,** 40 (1964).
99. Brubaker, G. R., Brown, J. N., Yoo, M. K., Kinsey, R. A., Kutchan, T. N., and Mottel, E. A., *Inorg. Chem.* **18,** 299 (1979).
100. Bew, M. J., Hathaway, B. J., and Feredy, R. J., *J. Chem. Soc. Dalton Trans.* 1229 (1972).
101. O'Young, C. L., Dewan, J. C., Lilienthal, H. R., and Lippard, S. J., *J. Am. Chem. Soc.* **100,** 7291 (1978).
102. Lewis, D. L., Hatfield, W. E., and Hodgson, D. J., *Inorg. Chem.* **11,** 2216 (1972).
103. Lewis, D. L., McGregor, K. T., Hatfield, W. E., and Hodgson, D. J., *Inorg. Chem.* **13,** 1013 (1974).
104. Ivarsson, G., *Acta Chem. Scand.* **A33,** 323 (1979).
105. Foley, J., Kennefick, D., Phelan, D., Tyagi, S., and Hathaway, B., *J. Chem. Soc. Dalton Trans.* 2333 (1983).
106. Ray, N., Tyagi, S., and Hathaway, B., *Acta Crystallogr. Sect. B* **38,** 1574 (1982).
107. Pajunen, A., *Suom. Kemistil. B* **40,** 32 (1967); *Chem. Abstr.* **67,** 15818e (1967).
108. Pajunen, A., *Ann. Acad. Sci. Fenn. Ser. A* **II,** 138 (1967).
109. Majeste, R. J., and Trepons, L. M., *Inorg. Chem.* **13,** 1062 (1974).
110. Hathaway, B. J., and Tomlinson, A. A. G., *Coord. Chem. Rev.* **5,** 1 (1970).
111. Ivarsson, G., *Acta Chem. Scand.* **27,** 3523 (1973).
112. Mohapatra, C. K. C., and Dash, K. C., *J. Inorg. Nucl. Chem.* **39,** 1253 (1977).
113. Fawcett, T. G., Rudich, S. M., Toby, B. H., Lalancette, R. A., Potenza, J. A., and Schugar, H. J., *Inorg. Chem.* **19,** 940 (1980).
114. Glick, M. D., Gavel, D. P., Diaddario, L. L., and Rorabacher, D. B., *Inorg. Chem.* **15,** 1190 (1976).
115. Sakaguchi, U., and Addison, A. W., *J. Chem. Soc. Dalton Trans.* 600 (1979).
116. Pajunen, A., Smolander, K., and Belinskij, I., *Suom. Kemistil. B* **45,** 317 (1972).
116a. Pajunen, A., and Lehtonen, M., *Suom. Kemistil. B* **45,** 43 (1972).
117. Olmstead, M. M., Musker, W. K., and Kessler, R. M., *Inorg. Chem.* **20,** 151 (1981).
118. Luukkonen, E., Pajunen, A., and Lehtonen, M., *Suom. Kemistil. B* **43,** 160 (1970).
118a. McWhinnie, W. R., *J. Inorg. Nucl. Chem.* **26,** 21 (1964).
118b. Procter, I. M., Hathaway, B. J., and Nicholls, P., *J. Chem. Soc. A* 1678 (1968).
119. Darriet, J., Haddad, M. S., Duesler, E. N., and Hendrickson, D. N., *Inorg. Chem.* **18,** 2679 (1979).
120. Sekizaki, M., Marumo, F., Yamasaki, K., and Saito, Y., *Bull. Chem. Soc. Jpn.* **44,** 1731 (1971).
121. Battaglia, L. P., Corradi, A. B., Marcotrigiano, G., Menabue, L., and Pellacani, G. C., *J. Chem. Soc. Dalton Trans.* 8 (1981).
122. West, D. X., *Inorg. Nucl. Chem. Lett.* **14,** 155 (1978).
123. Bonnett, P. J. J., and Jeannin, Y., *Acta Crystallogr. Sect. B* **26,** 318 (1970).
124. Ou, C. C., Miskowski, V. M., Lalancette, R. A., Potenza, J. A., and Schugar, H. J., *Inorg. Chem.* **15,** 3157 (1976).

125. Hussain, M. S., Joesten, M. D., and Lenhert, P. G., *Inorg. Chem.* **9,** 162 (1970).
126. Aoi, N., Matsubayashi, G., and Tanaka, T., *J. Chem. Soc. Dalton Trans.* 1059 (1983).
127. Chow, S. T., and McAuliffe, C. A., *Inorg. Nucl. Chem. Lett.* **8,** 913 (1972).
128. Bell, J. D., Freeman, H. C., Wood, A. M., Driver, R., and Walker, W. R., *J. Chem. Soc. Chem. Commun.* 1441 (1969).
129. Nelson, S. M., Esho, F. S., and Drew, M. G. B., *J. Chem. Soc. Dalton Trans.* 407 (1982).
130. Ivarsson, G., Lundberg, B. K. S., and Ingri, N., *Acta Chem. Scand.* **26,** 3005 (1972).
131. Dikhoff, T. G. M. H., and Goel, R. G., *Inorg. Chim. Acta* **44,** L72 (1980).
132. Udupa, M. R., and Padmanabhan, M., *Inorg. Chim. Acta* **13,** 289 (1975).
133. Guitard, A., Mari, A., Beauchamp, A. L., Dartiguenave, Y., and Dartiguenave, M., *Inorg. Chem.* **22,** 1603 (1983).
134. Bjork, N., and Cassel, A., *Acta Chem. Scand.* **A30,** 235 (1976).
135. Uson, R., Laguna, A., Laguna, M., and Perez, V., *Synth. Inorg. Met. Org. Chem.* **11,** 361 (1981).
136. Uson, R., Gimeno, J., Fornies, J., Martinez, F., and Fernandez, C., *Inorg. Chim. Acta* **63,** 91 (1982).
137. Uson, R., Royo, P., and Laguna, A., *Synth. Inorg. Met. Org. Chem.* **3,** 237 (1973).
137a. Uson, R., Laguna, A., and Vicente, J., *Synth. Inorg. Met. Org. Chem.* **7,** 463 (1977).
138. Uson, R., Laguna, A., and Sanjoaquin, J. L., *J. Organomet. Chem.* **80,** 147 (1974).
139. Naikar, S. B., Nanje Gowda, N. M., and Reddy, G. K. N., unpublished results.
140. Interrante, L. V., *Inorg. Chem.* **7,** 943 (1968).
141. Aleya, E. C., Dias, S. A., Ferguson, G., and Khan, M. A., *J. Chem. Res. Synop.* 360 (1979).
142. Naikar, S. B., Nanje Gowda, N. M., and Reddy, G. K. N., *Indian J. Chem.* **20A,** 436 (1981).
143. Aleya, E. C., Dias, S. A., Goel, R. G., Ogini, W. O., Pilon, P., and Meek, D. W., *Inorg. Chem.* **17,** 1697 (1978).
144. Davis, A. R., Murphy, C. J., and Plane, R. A., *Inorg. Chem.* **9,** 423 (1970).
145. Aleya, E. C., Dias, S. A., Ferguson, G., and Khan, M. A., *Can. J. Chem.* **57,** 2217 (1979).
146. Sandström, M., *Acta Chem. Scand.* **A32,** 527 (1978).
147. Epstein, J. M., Dewan, J. C., Kepert, D. L., and White, A. H., *J. Chem. Soc. Dalton Trans.* 1949 (1974).
148. Jones, T. E., Sokol, L. S. W. L., Rorabacher, D. B., and Glick, M. D., *J. Chem. Soc. Chem. Commun.* 140 (1979).
149. Karayannis, N. M., Bradshaw, E. E., Pytlewski, L. L., and Labes, M. M., *J. Inorg. Nucl. Chem.* **32,** 1079 (1970).
150. Karayannis, N. M., Owens, C., Pytlewski, L. L., and Labes, M. M., *J. Inorg. Nucl. Chem.* **31,** 2767 (1969).
151. Grandey, R. C., and Moeller, T., *J. Inorg. Nucl. Chem.* **32,** 333 (1970).
151a. Navaneetham, N. S., and Soundararajan, S., *Proc. Indian Acad. Sci. Sect. A* **90,** 439 (1981).
152. Ciampolini, M., Dapporto, P., and Nardi, N., *J. Chem. Soc. Dalton Trans.* 974 (1979).
153. Milburn, G. W. H., Truter, M. R., and Vickery, B. L., *J. Chem. Soc. Chem. Commun.* 1188 (1968).
154. Barkigia, K. M., Spaulding, L. D., and Fajer, J., *Inorg. Chem.* **22,** 349 (1983).

155. Matyashin, Yu. N., Kon'kova, T. S., Titova, K. V., Rasabvskii, V. Ya., and Lebedev, Yu. A., *Russ. J. Inorg. Chem.* **26,** 183 (1981).

156. Blundell, T. L., and Powell, H. M., *J. Chem. Soc. Chem. Commun.* 54 (1967).

157. Elder, R. C., Heeg, M. J., and Deutsch, E., *Inorg. Chem.* **17,** 427 (1978).

158. Clark, H. C., and O'Brien, R. J., *Inorg. Chem.* **2,** 740 (1963).

159. Belin, C., Chaabouni, M., Pascal, J. L., Potier, J., and Roziere, J., *J. Chem. Soc. Chem. Commun.* 105 (1980).

160. Ferguson, G., Goel, R. G., March, F. C., Ridley, G. A., and Prasad, H. S., *J. Chem. Soc. Chem. Commun.* 1547 (1971).

161. Ferguson, G., March, F. C., and Ridley, D. R., *Acta Crystallogr. Sect. B* **31,** 1260 (1975).

162. March, F. C., and Ferguson, G., *J. Chem. Soc. Dalton Trans.* 1291 (1975).