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TRANSITION METAL HYDROXYOXIME COMPLEXES

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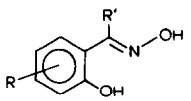
A. INTRODUCTION

Organic chelating ligands containing the oxime functional group have been used extensively in analytical chemistry for the detection or separation of metals [1–5]. Tschugaeff [1] first introduced dimethylglyoxime as a gravimetric reagent for nickel, and since then, analytical applications have been found for a variety of bidentate chelating oximes such as dioximes, acyloin oximes and aromatic *o*-hydroxyoximes [4]. Detailed historical accounts of the early development of oximes as analytical reagents have been written [4,6–8] and numerous reviews have appeared [9–18] on various aspects of the chemical properties of metal–oxime complexes including recent reviews on the structural chemistry of transition metal complexes [9,10,12] and O-organometallic derivatives of non-transition metals [12,13]. The purpose of this particular review is to address an increasingly important subset of the metal–oxime complexes, namely the hydroxyoxime complexes of transition metals.

Transition metal hydroxyoxime complex structural chemistry is of interest from two principal perspectives. First, from a fundamental analytical point of view, it is important to understand the nature of the bonding mechanisms in order to devise synthetic methods for the preparation of new metal–hydroxyoxime derivatives and to design more functional reagents for selective metal partitioning in applications of separation science. While successful development of truly selective chelating hydroxyoxime ligands has not yet been achieved, knowledge of the structural chemistry of a particular metal–hydroxyoxime system can provide valuable information for development of new and more efficient analytical reagents [19]. Secondly, hydroxyoximes are playing an increasingly important role as commercial reagents in extractive metallurgy, both in solvent extraction [19–27] and froth flotation [28–32]. Therefore, it is necessary to understand their coordination behavior in transition metal systems. The structural and electronic effects of modification of the organic backbone on chemical properties such as the ionization and coordination behavior of the hydroxyl and oxime functional groups, solubilities of the ligand and metal ligand complex and complex stability and reactivity must be carefully examined. For example, the presence of a nitro substituent at the three-position in 2-hydroxy-5-octylbenzophenone oxime permits extraction of Cu(II) from aqueous solution by the oxime at a significantly lower pH than by the parent oxime [20]. This lower pH functionality has been attributed to decreased oxygen–metal bond stability and increased π-acceptor ligand properties as a result of the electronic effects induced by the NO_2 group.

In this review, we have attempted to compile a comprehensive listing of transition metal–hydroxyoxime complexes which have been characterized by

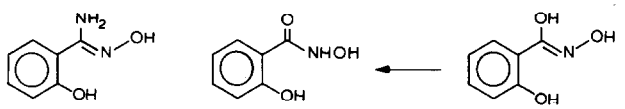
direct analytical methods and to discuss briefly the general structural chemistry of the hydroxyoxime complexes in terms of the characterization methods used. In the case of the salicylaldoxime derivatives it has been necessary to limit the discussion to only those hydroxyoximes in which the carbon adjacent to the oxime grouping contains either an alkyl or aryl substituent (**I**).



R' = H, alkyl or aryl only

I

This criterion has eliminated necessarily the salicylamidoximes (**II**) and the oxime tautomer (**IV**) of salicylhydroxamic acid (**III**).



II **III** **IV**

We briefly mention several of these complexes in a non-comprehensive section at the end of the review.

The review also includes the characterization of mixed ligand complexes of the type: metal/hydroxyoxime/other reagent where the "other reagent" includes HDNNS (i.e., dinonylnaphthalene sulfonic acid) and carboxylic acids (lauric acid, versatic acid, etc.). These hydroxime/other reagent mixtures are of considerable interest in metal extraction processes because they are not only capable of synergistic and/or selective extraction of metal ions such as Ni^{2+} [33–39], Co^{2+} [33–36,38] and Cu^{2+} [40,41] but also serve as models for the study of interfacial activity (including phase transfer catalysis and micellar catalysis) [42–44] and mixed complex formation (including adduct and ion pair formation) [33,45–47].

The transition metal hydroxyoxime complexes which we have surveyed are tabulated in Table 1. Complexes within this table are listed arbitrarily in order of the structural simplicity of the basic hydroxyoxime ligand, beginning with the aromatic *ortho*-hydroxyoximes and ending with the acyloin oximes. The transition metals are listed in succession within each group, starting with the earliest metal in the periodic table in its lowest oxidation state. The entries under each metal listing are further categorized according to the structure of the ligand. For the aromatic *o*-hydroxyoximes, the least substituted ligands are listed before the more substituted ones while the acyloin oximes are tabulated with the alkyl derivatives preceding the aryl and alkaryl compounds. For illustration, bis-(2-hydroxy-benzaldoximato)

TABLE 1

Transition metal–hydroxyoxime complexes

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
2-Hydroxy-benzaldoximes (H_2box)						
Titanium(IV)						
[Ti–(Hbox)]—yellow 1:1 complex reported (probably $[TiO(OH)(Hbox)]_2$)					Tit	49
$TiO(Hbox)_2$	Orange-yellow	Nujol: 3340 br m	Nujol: 1598 m	tbp	IR; PMR; elec; MW; elem anal; tit	48, 49
$TiO(R\text{–}Hbox)_2$ R = 3-Me	Orange-yellow	Nujol: 3340 br m	Nujol: 1590 m	tbp	IR; PMR; elec; MW; elem anal	48
$TiO(R\text{–}Hbox)_2$ R = 4-Me	Orange	Nujol: 3300 br m	Nujol: 1580 m	tbp	IR; PMR; elec; MW; elem anal	48
$TiO(R\text{–}Hbox)_2$ R = 5-Me	Orange-red	Nujol: 3340 br	Nujol: 1580 m	tbp	IR; PMR; elec; MW; elem anal	48
$TiO(X\text{–}Hbox)_2$ X = 5-Cl	Orange-red	Nujol: 3320 br m	Nujol: 1580 m	tbp	IR; PMR; elec; MW; elem anal	48
Vanadium(III)						
[V–(H_2box)]—brown complex reported (probably $V(OH)(Hbox)_2$)						50, 52
Vanadium(IV)						
$VO(Hbox)_2$	Brown	Nujol: 3200–3300 m br	Nujol: 1535 m	tbp	Elec; elem anal; IR; mag; UV-VIS; tit	51, 52
$VO(R\text{–}Hbox)_2$ R = 3-Me	Brown	Nujol: 3150–3250 m br	Nujol: 1552 m	tbp	Elec; elem anal; IR; mag; UV-VIS	51
$VO(R\text{–}Hbox)_2$ R = 4-Me	Brown	Nujol: 3280–3180 w br	Nujol: 1548 s	tbp	Elec; elem anal; IR; mag; UV-VIS	51
$VO(R\text{–}Hbox)_2$ R = 5-Me	Brown	Nujol: 3250–3180 m br	Nujol: 1545 s	tbp	Elec; elem anal; IR; mag; UV-VIS	51

$VO(X\text{–}Hbox)_2$ X = 5-Cl	Brown	Nujol: 3260–3190 m br	Nujol: 1550 s	tbp	Elec; elem anal; IR; mag; UV-VIS	51
Vanadium(V)						
$VO(OH)(Hbox)_2$	Violet	–	–	oct (*cis*)	Elem anal; mag; UV-VIS; tit	52
$Na[VO_2(Hbox)_2]$	Violet	–	–	oct (*cis*)	UV-VIS; tit	52
$Na_3[VO_2(box)_2]$	Violet	–	–	oct (*cis*)	UV-VIS; tit	52
Manganese(II)						
$[Mn(Hbox)]^+$	–	–	–	–	Elec; UV-VIS; graph; tit; mag	53, 55
$Mn(Hbox)_2$	Green- brown	–	Nujol: 1553	sp (*trans*)	Mag; tit; UV-VIS; graph; elem anal; IR	3, 54, 56, 256
$Na[MnH(box)_2]$	–	KBr: 3200	HCB: 1625	sp (*cis*)	Elem anal; IR; UV-VIS	55, 56
$Na[MnH(R\text{–}box)_2]$ R = 5-Me	–	KBr: 3250	HCB: 1632	sp (*cis*)	Elem anal; IR; UV-VIS	55
$Na[MnH(Y\text{–}box)_2]$ $Y = 5\text{-}NO_2$	Green- brown	KBr: 3300	HCB: 1629	sp (*cis*)	Elem anal; IR; UV-VIS	55, 256
$Na[MnH(X\text{–}box)_2]$ X = 5-Cl	Green- brown	KBr: 3250	HCB: 1629	sp (*cis*)	Elem anal; IR; UV-VIS	55, 256
Iron(II)						
$[Fe(Hbox)]^+$	–	–	–	–	UV-VIS; graph; tit, mag	54
$Fe(Hbox)_2$	Gray- purple	–	–	sp (*cis*)	UV-VIS; tit; Möss; mag; therm	54, 57, 87, 91
$Fe(Hbox)_2OH]^-$	–	–	–	–	UV-VIS; tit; mag; graph	54
$Na[FeH(box)_2]$	Brown	KBr: 3200	HCB: 1617	sp (*cis*)	Elem anal; IR; UV-VIS; Möss; mag	55, 87, 256
$Na[FeH(R\text{–}box)_2]$ R = 5-Me	–	KBr: 3000	HCB: 1632	sp (*cis*)	Elem anal; IR; UV-VIS; Möss; mag	55, 87
$Na[FeH(Y\text{–}box)_2]$ $Y = 5\text{-}NO_2$	Green- brown	KBr: 3250	HCB: 1630	sp (*cis*)	Elem anal; IR; UV-VIS; Möss; mag	55, 87, 256

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
$Na[FeH(X\text{–box})_2]$ X = 5-Cl	Green-brown	KBr: 3200	HCB: 1627	sp (*cis*)	Elem anal; IR; UV-VIS; Möss; mag	31, 48, 256
Iron(III)						
$[Fe(H_2box)]^{3+}$	Blue	–	–	–	UV-VIS; graph	88, 89
$[Fe(Hbox)]^{2+}$	–	–	–	–	UV-VIS; graph	58
$Fe(Hbox)_3$	–	–	–	–	UV-VIS; graph	58
$[FeOH(H_2box)^{2+}$	Violet	–	–	–	UV-VIS; graph	88, 89
$[Fe(OH)_2(H_2box)]^+$	Violet	–	–	–	UV-VIS; graph	88, 89
$[Fe(OH)_3(H_2box)]$	Yellow-brown	–	–	–	UV-VIS; graph	88, 89
$[Fe(OH)(Hbox)_2]_2$	Dark brown	–	–	dimeric	Mag; IR; Möss; elem anal	59
$[Fe(OH)(R\text{–}Hbox)_2]_2$ R = 3-MeO	Dark brown	–	–	dimeric	Mag; IR; Möss; elem anal	59
$Fe(OH)_2(R\text{–}Hbox)$ R = 3-MeO	Dark reddish brown	–	–	polymeric	Mag; IR; Möss; elem anal	59
$Fe(R\text{–}Hbox)_3$ R = 3-COOH	Orange-red	–	–	–	UV-VIS; graph	89, 90
Cobalt(II)						
$[Co(Hbox)]^+$	–	–	–	–	UV-VIS; tit; mag; graph	54
$Co(Hbox)_2$	Red-brown	–	Nujol: 1550	sp (*trans*)	Elem anal; UV-VIS; mag; IR; tit; graph	26, 54, 56, 87, 92–98
$Na[CoH(box)_2]$	–	KBr: 3050	HCB: 1625	sp (*cis*)	Elem anal; IR; UV-VIS; mag	55, 87
$Na[CoH(R\text{–}box)_2]$ R = 5-Me	–	KBr: 3000	HCB: 1644	sp (*cis*)	Elem anal; IR; UV-VIS; mag	55, 87
$Na[CoH(Y\text{–}box)_2]$ Y = 5-NO_2	Green	KBr: 3200	HCB: 1638	sp (*cis*)	Elem anal; IR; UV-VIS; mag	55, 87, 256

$Na[CoH(X\text{-box})_2]$ X = 5-Cl	Brown	KBr: 3200	HCB: 1627	sp (*cis*)	Elem anal; IR; UV-VIS; mag	55, 87, 256
Cobalt(III)						
$[Co_2(Hbox)_3]$	–	–	–	–	Tit; graph; UV-VIS	99
Nickel(II)						
$[Ni(Hbox)]^+$	–	–	–	–	UV-VIS; tit; mag; graph	54
$Ni(Hbox)_2$	Green	KBr: 2950	HCB: 1650 Nujol: 1558	sp (*trans*)	Elem anal; UV-VIS; mag; IR; tit; graph; MW; therm; X-ray; grav	26, 46, 47, 54–56, 60–64, 87, 91, 92, 95, 99–109, 256, 258, 283
$Ni(Hbox)_2Y_2$ Y = pyridine (C_5H_5–N)	Yellow- ish white	–	–	oct	Elem anal; UV-VIS; mag; grav	46, 47, 60–63
$Ni(Hbox)_2Y_2$ Y = 2-, 3-, 4-CH_3	–	–	–	oct	UV-VIS; mag; grav	47, 63
$Ni(Hbox)_2Y_2$ Y = $(CH_2)_nNH$, *n* = 2, 3, 4, 5, 6	–	–	–	oct	UV-VIS; mag; grav	47, 64
$Ni(Hbox)_2Y_2$ Y = 3-, 4-, pipecoline	–	–	–	oct	UV-VIS; mag; grav	47
$Ni(Dbox)_2$	Green	–	–	sp (*trans*)	IR	56
$K_2[Ni(box)_2]\cdot 2$ EtOH	Green- yellow	–	–	–	Elem anal; mag; tit; UV-VIS; graph	99, 104, 258
$Ni(R\text{-}Hbox)_2$ R = 5-Me	Green	KBr: 2950	HCB: 1650	sp (*trans*)	Elem anal; IR; UV-VIS; mag; graph; tit	54, 55, 87
$Ni(RR\text{-}Hbox)_2$ R = 5-C_9H_{19}	–	–	–	sp	Elem anal; IR; UV-VIS	65
$Ni(Y\text{-}Hbox)_2$ Y = 5-NO_2	Green	KBr: 3435 m s 3100 s	HCB: 1633	sp (*trans*)	Elem anal; IR; UV-VIS; mag; graph; tit; therm	54, 55, 87, 91, 256
$Ni(X\text{-}Hbox)_2$ X = 5-Cl	Green	KBr: 3000	HCB: 1649	sp (*trans*)	Elem anal; IR; UV-VIS; mag; graph; tit	54, 55, 87, 256

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
$Ni(R-Hbox)_2$ R = 3-MeO	Green	–	–	–	Elem anal; grav	110
$Ni(R-Hbox)_2$ R = 3-COOH	Green	–	–	sp (*trans*)	Elem anal; tit; grav	89, 111
$Ni(R-Hbox)_2 \cdot H_2O$ R = 4-OH	Green	–	–	–	Elem anal; mag; grav	112
$Ni(R-Hbox)_2$ R = 5-OH	Green	–	–	–	Elem anal; grav	113
$Ni(R-Hbox)_2$ R = 5-MeO	Green	–	–	–	Elem anal; grav	113
$Ni(R-Hbox)_2$ R = 5-PhN=N	Green	KBr:	KBr: 1605	sp (*trans*)	Elem anal; mag; grav; IR; therm; MW	114
Copper(II)						
$Cu(Hbox)_2$	Green-yellow	KBr: 3050	HCB: 1658 Nujol: 1600 s	sp (*trans*)	Elem anal; UV-VIS; mag; IR; tit; graph; MW; therm; X-ray; EPR; grav	3, 26, 54–56, 58, 91, 95, 97, 99, 115–121, 256, 282
$[Cu(box)_2]^{2-}$	–	–	–	–	UV-VIS; tit; graph	99
$Cu(R-Hbox)_2$ R = 3-Me	Green	–	–	–	Elem anal; grav	110
$Cu(R-Hbox)_2$ R = 5-C_9H_{19}	–	–	–	–	UV-VIS; IR	65
$Cu(R-Hbox)_2$ R = 3-COOH	Green-yellow	–	–	sp (*trans*)	Elem anal; tit; grav	89, 111
$Cu(R-Hbox)_2 \cdot H_2O$ R = 4-OH	Green-gray	–	–	–	Elem anal; mag; grav	112
$Cu(R-Hbox)_2$ R = 5-OH	Green	–	–	–	Elem anal; grav	113

$Cu(R\text{–}Hbox)_2$ R = 5-Me	Green	KBr: 3050	HCB: 1652 Nujol: 1660 s	sp (*trans*)	Elem anal; IR; UV-VIS: mag; graph; tit	54, 55
$Cu(R\text{–}Hbox)_2$ R = 5-MeO	Green	–	–	–	Elem anal; grav	113
$Cu(Y\text{–}Hbox)_2$ Y = 5-NO_2	Green	KBr: 3435 m s 3100 s	HCB: 1633	sp (*trans*)	Elem anal; IR; UV-VIS; mag; graph; tit; therm	54, 55, 91, 256
$Cu(X\text{–}Hbox)_2$ X = 5-Cl	Green	KBr: 3100	HCB: 1649	sp (*trans*)	Elem anal; IR; UV-VIS; mag; graph; tit; X-ray	54, 55, 122, 256
$Cu(R\text{–}Hbox)_2$ R = 5-t-Bu	Yellow	–	–	–	UV-VIS; graph	123
$Cu(R\text{–}Hbox)_2$ R = 5-PhN=N	Green- brown	–	KBr: 1607	sp (*trans*)	Elem anal; mag; IR; therm; MW; grav	114
Zinc(II)						
$[Zn(Hbox)]^+$	–	–	–	–	UV-VIS; tit; mag; graph	54
Zn(box)	Yellow- white	–	–	–	Elem anal; X-ray; therm	115, 124–128
$Zn(Hbox)_2$	Yellow	–	–	–	Elem anal; X-ray; therm; tit; mag; UV-VIS; graph	54, 124, 129, 256
$Na[ZnH(box)_2]$	–	KBr: 3300	HCB: 1624	sp (*cis*)	Elem anal; IR; UV-VIS; tit	55
$Na[ZnH(R\text{–}box)_2]$ R = 5-Me	–	KBr: 2950	HCB: 1634	sp (*cis*)	Elem anal; IR; UV-VIS; tit	55
$Na[ZnH(Y\text{–}box)_2]$ Y = 5-NO_2	Yellow- white	–	HCB: 1654	sp (*cis*)	Elem anal; IR; UV-VIS; tit	55, 256
$Na[ZnH(X\text{–}box)_2]$ X = 5-Cl	Yellow- white	KBr: 3300	HCB: 1635	sp (*cis*)	Elem anal; IR; UV-VIS; tit	55, 256
Yttrium(III)						
$Y(Hbox)X_2 \cdot 2\ H_2O$ X-Cl	–	Nujol: 3650 s m	Nujol: 1640 s	oct	Elem anal; IR; UV-VIS	179
$Y(R\text{–}Hbox)_2X \cdot 2\ H_2O$ R = 3-MeO; X = Cl	–	Nujol: 3150 s m	Nujol: 1630	oct	Elem anal; IR; UV-VIS	179

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
Zirconium(IV)						
[Zr–(Hbox)]—white 1:1 complex reported (probably $[ZrO(OH)(Hbox)]_2$)					Tit	49
Niobium(V)						
[Nb–(Hbox)]—yellow complex reported (probably $NbO(OH)(Hbox)_2$]					Grav	130
Molybdenum(VI)						
$MoO_2(Hbox)_2$	Yellow-orange	–	–	–	UV-VIS; tit; grav	131
$MoO_2(R–Hbox)_2$ R = 5-MeO	Yellow-orange	–	–	–	UV-VIS	132
Rhodium(I)						
$Rh(Hbox)_2(CO)_2$	Orange-yellow	–	–	–	Elem anal; MW; IR; elec	281
Palladium(II)						
$Pd(Hbox)_2$	Yellow	–	HCB: 1608 vs	sp (*trans*)	Elem anal; IR; UV-VIS; X-ray; grav; therm; MW; tit	56, 97, 101, 102, 115, 133–136
$[Pd(Hbox)X]_2$ X = Cl	Brown	–	–	dimeric	Elem anal	101, 136
$Pd(R–Hbox)_2$ R = 3-MeO	Yellow	–	–	–	Elem anal; therm; grav	137, 138
$Pd(R–Hbox)_2$ R = 5-OH	–	–	–	–	Elem anal; grav	113
$Pd(R–Hbox)_2$ R = 5-MeO	Yellow	–	–	–	Elem anal; grav	113
$Pd(X–Hbox)_2$ X = 5-Cl	Yellow	–	–	sp (*trans*)	X-ray	134
Cadmium(II)						
Cd(box)	Yellow	KBr: 3420 wbr	KBr: 1600 vs	–	Elem anal; therm; mass; tit	66

$Cd(Hbox)_2$	White	KBr: 3502 m	KBr: 1599 s	sp (*trans*)	Elem anal; therm; mass; tit; IR	66, 95
Lanthanum(III)						
$La(Hbox)X_2 \cdot 2\ H_2O$ X = Cl	–	Nujol: 3250–3150	Nujol: 1625	–	Elem anal; IR; UV-VIS	179
$La(R\text{–}Hbox)_2X \cdot 2\ H_2O$ R = 3-MeO; X = Cl	–	Nujol: 3380–3300	Nujol: 1630 s m	–	Elem anal; IR; UV-VIS	179
Cerium(IV)						
$Ce(Hbox)_2Y_2 \cdot 2\ H_2O$ Y = NO_3	–	–	–	–	Elem anal; UV-VIS	179
$Ce(R\text{–}Hbox)_4 \cdot 2\ H_2O$ R = 3-MeO	–	Nujol: 3345–3140	Nujol: 1640 s m	–	Elem anal; IR; UV-VIS	179
Praseodymium(III)						
$Pr(Hbox)X_2 \cdot 2\ H_2O$ X = Cl	–	Nujol: 3800	Nujol: 1590 s m	–	Elem anal; IR; UV-VIS	179
$Pr(R\text{–}Hbox)_2X \cdot 2\ H_2O$ R = 3-MeO; X = Cl	–	Nujol: 3180–3140 b	Nujol: 1635 s m	–	Elem anal; IR; UV-VIS	179
Neodymium(III)						
$Nd(Hbox)X_2 \cdot 2\ H_2O$ X = Cl	–	Nujol: 3350	Nujol: 1620	–	Elem anal; IR; UV-VIS	179
$Nd(R\text{–}Hbox)_2X \cdot 2\ H_2O$ R = 3-MeO; X = Cl	–	Nujol: 3340	Nujol: 1645	–	Elem anal; IR; UV-VIS	179
Samarium(III)						
$Sm(Hbox)X_2 \cdot 2\ H_2O$ X = Cl	–	Nujol: 3300 s m	Nujol: 1620	–	Elem anal; IR; UV-VIS	179
$Sm(R\text{–}Hbox)_2X \cdot 2\ H_2O$ R = 3-MeO; X = Cl	–	Nujol: 3360 m	Nujol: 1625	–	Elem anal; IR; UV-VIS	179
Gadolinium(III)						
$Gd(Hbox)X_2 \cdot 2\ H_2O$ X = Cl	–	Nujol: 3500	Nujol: 1625	–	Elem anal; IR; UV-VIS	179
$Gd(R\text{–}Hbox)_2X \cdot 2\ H_2O$ R = 3-MeO; X = Cl	–	Nujol: 3310	Nujol: 1650	–	Elem anal; IR; UV-VIS	179

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
Hafnium(IV)						
[Hf–(Hbox)]—white 1:1 complex reported (probably $[HfO(OH)(Hbox)]_2$)					Tit	49
Platinum(II)						
$Pt(Hbox)_2$	Yellow	–	–	sp (*trans*)	Elem anal; MW; X-ray	101
$Pt(H_2box)_2X_2$ X = Cl	Yellow-green	–	–	–	Elem anal	101
Uranium(VI)						
$UO_2(Hbox)_2$	Orange-yellow	Nujol: 3205 br m	Nujol: 1525 s	oct (*trans*)	Elem anal; IR; Elec	139
$UO_2(R–Hbox)_2$ R = 3-Me	Orange-yellow	Nujol: 3180 br m	Nujol: 1525 s	oct (*trans*)	Elem anal; IR; elec	139
$UO_2(OH)(R–Hbox)(H_2O)$ R = 3-COOH	Orange-red	–	–	oct	Graph; UV-VIS; grav	89, 111, 140
$UO_2(R–Hbox)_2$ R = 4-Me	Orange	Nujol: 3200 br m	Nujol: 1535 s	oct (*trans*)	Elem anal; IR; elec	139
$UO_2(R–Hbox)_2$ R = 5-Me	Orange	Nujol: 3200 br m	Nujol: 1535 s	oct (*trans*)	Elem anal; IR; elec	139
$UO_2(X–Hbox)_2$ X = 5-Cl, NO_2	Orange	–	–	–	–	256
2-Hydroxy-alkylphenone oxime ($H_2R'pox$)						
Titanium(IV)						
$[TiO(OH)(R'Hpox)]_2$ R′ = Me	Yellow	–	–	dimeric	Grav	141, 142
$TiO(R'Hpox)_2$ R′ = Me	Orange-yellow	Nujol: 3300 br w	Nujol: 1535 s	tbp	Elem anal; IR; elec; MW	143
$TiO(R–R'Hpox)_2$ R = 3-Me; R′ = Me	Orange-yellow	Nujol: 3300 br w	Nujol: 1535 s	tbp	Elem anal; IR; elec; MW	143
$TiO(R–R'Hpox)_2$ R = 4-Me; R′ = Me	Orange	Nujol: 3300 br w	Nujol: 1550 s	tbp	Elem anal; IR; elec; MW	143

$TiO(R–R'Hpox)_2$ R = 5-Me, R′ = Me	Orange-red	Nujol: 3300 br w	Nujol: 1538 s	tbp	Elem anal; IR; elec; MW	143
$[TiO(OH)(R–R'Hpox)]_2$ R = 5-Me; R′ = Me, Et, Pr	Red-yellow	–	–	dimeric	Tit; MW; mag	144
$TiO(X–R'Hpox)_2$ X = 5-Cl; R′ = Me	Orange-red	Nujol: 3300 br w	Nujol: 1538 s	tbp	Elem anal; IR; elec; MW	143
$[Ti(OH)_2(X–R'Hpox)]_2$ X = 5-Cl; R′ = Me	Red-yellow	–	–	dimeric	Grav	145
$[TiO(OH)(R–R'Hpox)]_2$ R = 4-Me; R′ = Et	Yellow	–	–	dimeric	Elem anal; MW; mag; UV-VIS; grav	146
$[TiO(OH)(R–R'Hpox)]_2$ R = 5-Me; R′ = Et	yellow-red	–	–	dimeric	Elem anal; MW; mag; grav	147
Vanadium(IV)						
$VO(R'Hpox)_2$ R′ = Me	Red-brown	KBr: 3300 s	KBr: 1548 s	spy	Elem anal; IR; UV-VIS; elec; mag; tit	148, 149
$VO(R–R'Hpox)_2$ R = 3-Me; R′ = Me	Red-brown	KBr: 3290	KBr: 1550	spy	Elem anal; IR; mag; UV-VIS; elec; tit	148, 149
$VO(X–R'Hpox)_2$ X = 3-Cl; R′ = Me	Brown	–	–	–	Tit	149
VO(R–R′Hpox) R = 4-Me; R′ = Me	Red-brown	KBr: 3300	KBr: 1550 s	spy	Elem anal; IR; UV-VIS; elec; mag; tit	148, 149
$VO(R–R'Hpox)_2$ R = 5-Me; R′ = Me	Red-brown	KBr: 3170 s	KBr: 1550 s	spy	Elem anal; IR; UV-VIS; elec; mag	148
$VO(X–R'Hpox)_2$ X = 5-Cl; R′ = Me	Red-brown	KBr: 3220 s	KBr: 1545	spy	Elem anal; IR; UV-VIS; elec; mag; tit	148, 149
$VO(X–R'Hpox)_2$ X = 5-Br, I, NO_2 R′ = Me	Brown	–	–	–	Tit	149
VO(R,X–R′Hpox) R = 4-Me, X = 5-Cl; R′ = Et	Brown	–	–	oct	Elem anal; mag	150
$VO(R–R'Hpox)_2$ R = 4-OH; R′ = Bu	–	–	–	–	IR	161

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
Vanadium(V)						
$VO(OH)(R'Hpox)_2$ R′ = Me	Red-brown	–	–	oct	Elem anal; mag; UV-VIS; grav	151–153
$VO(OH)(R–R'Hpox)_2$ R = 4-Me; R′ = Me	Red-brown	–	–	–	–	154
$VO(OH)(R–R'Hpox)_2$ R = 5-Me; R′ = Me	Red-brown	–	–	oct (*trans*)	MW; tit; mag	144
$VO(OH)(X–R'Hpox)_2$ X = 5-Cl; R′ = Me	Red-yellow	3500	1493	oct	Elem anal; IR; therm; grav	155
$VO(OH)(X,X'–R'Hpox)_2$ X = 3-Cl; X = 5-Cl R′ = Me	Yellow	–	–	–	UV-VIS; IR; tit	156
$VO(OH)(R,X–R'Hpox)_2$ R = 4-Me; X = 5-Cl R′ = Me	Yellow	–	–	–	UV-VIS; IR; tit	156
$VO(OH)(R–R'Hpox)_2$ R = 4-Me; R′ = Et	Red-brown	2980	1605	oct	Elem anal; IR; grav; mag; MW; graph	157
$VO(OH)(R–R'Hpox)_2$ R = 5-Me; R′ = Et	Red-brown	–	–	oct (*trans*)	Elem anal; mag; MW; tit	144, 158–160
$VO(OH)(R–R'Hpox)_2$ R = 5-Me; R′ = Pr	Red-brown	–	–	oct (*trans*)	MW; tit; mag	144
Manganese(II)						
$Mn(R'Hpox)_2$ R′ = Me	Green-yellow	–	–	–	Tit	151, 162
$Mn(R–R'Hpox)_2$ R = 3-Me, 4-OH, 4-Me, 5-Me; R′ = Me	Green-yellow	–	–	–	Tit	162
$Mn(X–R'Hpox)_2$ X = 3-Br, Cl, 5-Br, Cl, I; R′ = Me	–	–	–	–	Tit	162

$Mn(R-R'Hpox)_2$ R = 4-MeO; R′ = Me	–	–	–	–	Tit	164
$Mn(Y-R'Hpox)_2$ Y = 5-NO_2; R′ = Me	–	–	–	–	Tit	162
$Mn(Y-R'Hpox)_2$ Y = 5-NO_2; R′ = Et	–	–	–	–	Tit	163
Iron(II)						
Fe(R′pox) R′ = Me	–	–	–	–	UV-VIS; grav; graph; mag	278
Fe(R′pox) R′ = Et	–	–	–	–	UV-VIS; graph; grav; mag	279
Iron(III)						
$[Fe(R'Hpox)]^{2+}$ R′ = Me	Violet	–	–	–	UV-VIS; graph	165
$[Fe(R'R'Hpox)]^{2+}$ R = 4-OH; R′ = Me	Violet	–	–	–	UV-VIS; graph	166–168
$[Fe(X,X'-R'Hpox)]^{2+}$ X = 3-Cl; X′ = 5-Cl R′ = Me	Purple	–	–	–	UV-VIS	169
$Fe(X,X'-R'Hpox)_3$ X = 3-Cl; X′ = 5-Cl R′ = Me	Orange-red	–	–	oct	UV-VIS	169
$Fe(Y,R-R'Hpox)_3$ Y = 3-NO_2; R = 5-Me R′ = Me	Red-orange	–	–	oct	UV-VIS; mag; graph	170
$[Fe(R'Hpox)]^{2+}$ R′ = Et	Purple	–	–	–	UV-VIS; graph	171, 172
$[Fe(R-R'Hpox)]^{2+}$ R = 4-OH; R′ = Et	Violet	–	–	–	UV-VIS; graph	172–174
$[Fe(R-R'Hpox)]^{2+}$ R = 5-Me; R′ = Et	Blue	–	–	–	UV-VIS; graph	175
$Fe(R-R'Hpox)_3$ R = 5-Me; R′ = Et	Red-brown	–	–	oct	UV-VIS; graph	175

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
$[Fe(R'Hpox)]^{2+}$ R′ = Pr	Violet	–	–	–	UV-VIS; graph	171, 172, 176
$[Fe(R–R'Hpox)]^{2+}$ R = 4-OH; R′ = Pr	Violet	–	–	–	UV-VIS; graph	172, 177
$[Fe(R–R'Hpox)]^{2+}$ R = 4-OH; R′ = Bu	Purple	–	–	–	UV-VIS; graph	173, 178
Cobalt(II)						
$Co(R'Hpox)_2$ R′ = Me	Red-brown	–	–	sp	Tit	151, 162
$Co(R–R'Hpox)_2$ R = 3-Me; R′ = Me	Brown	–	–	sp	Tit	162
$Co(X–R'Hpox)_2$ X = 3-Cl; R′ = Me	Brown	–	–	sp	UV-VIS; mag; tit; IR; Elem anal; elec	162, 180
$Co(X–R'Hpox)_2$ X = 3-Br; R′ = Me	Brown	–	–	sp	Tit	162
$Co(R–R'Hpox)_2$ R = 4-OH; R′ = Me	Brown	–	–	sp	Tit	162, 181
$Co(R–R'Hpox)_2$ R = 4-MeO; R′ = Me	Brown	–	–	sp	Tit	164
$Co(R–R'Hpox)_2$ R = 5-Me; R′ = Me	Orange-yellow	–	–	sp (*trans*)	Elem anal; mag; grav; MW; tit; therm	144, 162, 182
$Co(X–R'Hpox)_2$ X = 5-Cl; R′ = Me	Yellow-orange	–	–	sp	Elem anal; mag; tit; UV-VIS; IR; elec	162, 180
$Co(X–R'Hpox)_2$ X = 5-Br, I, NO_2 R′ = Me	Yellow-orange	–	–	sp	Tit	162
$Co(R–R'Hpox)_2$ R = 5-C_9H_{19}; R′ = Me	Orange-yellow	–	–	–	IR; MW; therm	190
$Co(R,R''–R'Hpox)_2$ R = 3-Me, R″ = 5-Me; R′ = Me	–	–	–	–	Grav	67

$Co(X,X'-R'Hpox)_2$ X = 3-Cl; X' = 5-Cl R' = Me	Yellow-orange	–	KBr: 1550	sp (*trans*)	Elem anal; UV-VIS; mag; IR; elec; graph	180, 183–185
$Co(R-R'Hpox)_2$ R = 4-Me; R' = Et	–	–	–	–	Elem anal	217, 218
$Co(R-R'Hpox)_2$ R = 5-Me; R' = Et	Yellow-orange	–	–	sp (*trans*)	Elem anal; mag; MW; tit; UV-VIS; graph; grav	144, 159, 160, 186, 187
$Co(Y-R'Hpox)_2$ Y = 5-NO_2; R' = Et	–	–	–	–	Tit	188
$Co(R-R'Hpox)_2$ R = 5-Me; R' = Pr	Yellow-orange	–	–	sp (*trans*)	MW; mag; tit	144
$Co(R-R'Hpox)_2$ R = 4-OH; R' = Bu	Brown	KBr: 3500 b; 3280	KBr: 1600	sp (*trans*)	Elem anal; tit; elec; IR; graph	178, 189
Cobalt(III)						
$Co(R'Hpox)(R'pox)$ R' = C_7H_{15}	–	–	–	oct	UV-VIS	68
$Co(R-R'Hpox)(R-R'pox)$ R = 5-Me; R' = C_7H_{15}	–	–	–	oct	UV-VIS	68
Nickel(II)						
$Ni(R'Hpox)_2$ R' = Me	Green	3260	1540	sp (*trans*)	Elem anal; mag; UV-VIS; tit; IR; grav	151, 162, 191–194, 274
$Ni(R-R'Hpox)_2$ R = 3-Me; R' = Me	Green	–	–	sp	Tit	162
Ni(X–R'Hpox) X = 3-Cl, 5-Cl, Br R' = Me	Green	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; mag; UV-VIS; tit; IR; therm; X-ray; elec	162, 193
$Ni(X-R'Hpox)_2$ X = 3-Br, I; R' = Me	Green	–	–	sp	Tit	162
$Ni(R-R'Hpox)_2$ R = 4-OH; R'-Me	Green	–	–	sp	Elem anal; UV-VIS; tit; graph; therm; sol	162, 187, 195–199

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
Ni(R–R'Hpox)$_2$ R = 4-Me; R' = Me	Green	–	–	sp	Elem anal; MW; graph; grav	200
Ni(R–R'Hpox)$_2$ R = 4-MeO; R' = Me	Green	–	–	sp	Tit	164
Ni(R–R'Hpox)$_2$ R = 4-Pr; R' = Me	Green	–	–	–	Elem anal	201
Ni(X–R'Hpox)$_2$ X = 4-Cl; R' = Me	Green	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; IR; UV-VIS; mag; therm; X-ray; elec	193
Ni(R–R'Hpox)$_2$ R = 5-OH; R' = Me	Green	–	–	–	Tit	202
Ni(R–R'Hpox)$_2$ R = 5-Me; R' = Me	Green	3260	1535	sp (*trans*)	Elem anal; MW; mag; tit; IR; grav	144, 182, 274
Ni(R–R'Hpox)$_2$ R = 5-MeO; R' = Me	Green	–	–	sp (*trans*)	–	203
Ni(X–R'Hpox)$_2$ X = 5-Cl; R' = Me	Green	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; UV-VIS; mag; tit; IR; elec; therm; X-ray	162, 193
Ni(X–R'Hpox)$_2$ X = 5-Br, I, NO_2; R' = Me	Green	–	–	sp	Tit	162
Ni(R–R'Hpox)$_2$ R = 5-C_9H_{19}; R' = Me	Green	–	–		IR; MW; therm; UV-VIS; graph; elem anal	65, 190
Ni(R,R''–R'Hpox)$_2$ R = 3-Me; R'' = 5-Me; R' = Me	–	–	–	–	Grav	67
Ni(Y,R–R'Hpox)$_2$ Y = 3-NO_2; R = 5-Me R' = Me	Green	–	–	sp	–	204
Ni(X,X'–R'Hpox)$_2$ X = 3-Cl; X' = 5-Cl R' = Me	Green	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; IR; UV-VIS; mag; therm; tit; X-ray; elec	162, 184, 185, 193

$Ni(R,Y–R'Hpox)_2$ R = 4-OH; Y = 5-NO_2 R' = Me	Green	KBr: 3400–3600	KBr: 1630	sp (*trans*)	Elem anal; mag; UV-VIS; IR; X-ray	205
$Ni(R,X–R'Hpox)_2$ R = 4-Me; X = 5-Cl R' = Me	Green	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; IR; UV-VIS; mag; therm; tit; X-ray; elec	193, 206, 207
$Ni(R–R'Hpox)_2$ R = 4-OH; R' = Et	Yellow-green	–	–	–	Elem anal; grav	208
$Ni(R–R'Hpox)_2$ R = 4-Me; R' = Et	Yellow-green	–	–	–	Elem anal	217, 218
$Ni(R–R'Hpox)_2$ R = 5-Me; R' = Et	Yellow-green	–	–	sp (*trans*)	Elem anal; MW; mag; UV-VIS; grav; graph; tit	144, 159, 160, 186, 187, 209
$Ni(Y–R'Hpox)_2$ Y = 5-NO_2; R' = Et	Green	–	–	–	Tit	188
$Ni(R,Y–R'Hpox)_2$ R = 4-Me; Y = 5-Cl R' = Et	Green	–	–	sp	Elem anal; mag	150
$Ni(R–R'Hpox)_2$ R = 4-OH; R' = Pr	Yellow-green	–	–	–	Elem anal; grav	210
$Ni(R–R'Hpox)_2$ R = 5-Me; R' = Pr	Green	–	–	sp (*trans*)	MW; mag; tit	144
$Ni(R–R'Hpox)_2$ R = 4-OH; R' = Bu	Green	KBr: 3500 b 3280	KBr: 1600	sp (*trans*)	Elem anal; UV-VIS; elec; IR; tit; graph; grav	178, 211
Copper(II)						
$Cu(R'Hpox)_2$ R' = Me	Green-yellow	3260	1560	sp (*trans*)	Elem anal; mag; tit; UV-VIS; IR; grav	151, 162, 191, 192, 212, 274
$Cu(R–R'Hpox)_2$ R = 3-Me; R' = Me	Green	–	–	sp	Tit	162
$Cu(X–R'Hpox)_2$ X = 3-Cl, 5-Cl, Br R' = Me	Yellow	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; mag; EPR; UV-VIS; tit; IR; therm; X-ray; elec	162, 193
$Cu(X–R'Hpox)_2$ X = 3-Br,I; R' = Me	Yellow	–	–	sp	Tit	162

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
$Cu(R-R'Hpox)_2$ R = 4-OH; R′ = Me	Yellow	–	–	sp (*cis*)	UV-VIS; tit; graph; therm; sol	162, 181, 195, 197–199, 213
$Cu(R-R'Hpox)_2$ R = 4-MeO; R′ = Me	Yellow	–	–	sp	Tit	164
$Cu(X-R'Hpox)_2$ X = 4-Cl; R′ = Me	Yellow	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; IR; UV-VIS; mag; therm; X-ray; elec; EPR; tit	193
$Cu(R-R'Hpox)_2$ R = 5-Me; R′ = Me	Yellow-white	3260	1540	sp (*trans*)	Elem anal; MW; IR; UV-VIS; mag; EPR; tit; therm; elec; grav	144, 182, 203, 214, 274
$Cu(R-R'Hpox)_2$ R = 5-C_9H_{19}; R′ = Me	Yellow-white	–	–	–	IR; therm; MW; UV-VIS; graph; elem anal	65, 190
$Cu(R,R''-R'Hpox)_2$ R = 3-Me; R″ = 5-Me R′ = Me	–	–	–	–	grav	67
$Cu(R,R''-R'Hpox)_2$ R = 3-OH; R″ = 4-OH R′ = Me	Yellow-white	–	–	–	Grav	215
$Cu(Y,R-R'Hpox)_2$ Y = 3-NO_2; R = 5-Me R′ = Me	Yellow-white	–	–	sp	–	204
$Cu(X,X'-R'Hpox)_2$ X = 3-Cl; X′ = 5-Cl R′ = Me	Yellow-white	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; IR; UV-VIS; mag; therm; tit; EPR; X-ray; elec	162, 184, 185, 193
$Cu(R,Y-R'Hpox)_2$ R = 4-OH; Y = 5-NO_2 R′ = Me	Yellow-white	KBr: 3440; 3220; 3100	KBr: 1630	sp (*trans*)	Elem anal; mag; UV-VIS; IR; X-ray	205

$Cu(R,X–R'Hpox)_2$ R = 4-Me; X = 5-Cl R′ = Me	Yellow-white	KBr: 3160–2900	KBr: 1540–1520	sp (*trans*)	Elem anal; IR; UV-VIS; mag; therm; tit; EPR; X-ray; elec	193, 206, 207
$Cu(R–R'Hpox)_2$ R = 4-OH; R′ = Et	Brown	–	–	–	Elem anal; grav	216
$Cu(R–R'Hpox)_2$ R = 4-Me; R′ = Et	Yellow-white	–	–	–	Elem anal; MW; graph; UV-VIS	217, 218
$Cu(R–R'Hpox)_2$ R = 5-Me; R′ = Et	Yellow-white	–	–	sp (*trans*)	Elem anal; mag; grav; MW; tit; UV-VIS; graph; EPR; therm; elec	144, 159, 160, 186, 187, 214
$Cu(R,Y–R'Hpox)_2$ R = 4-Me; Y = 5-Cl R′ = Et	Yellow-white	–	–	sp	Elem anal; mag	150
$Cu(R–R'Hpox)_2$ R = 5-Me; R′ = Pr	Yellow-white	–	–	sp (*trans*)	MW; mag; tit; UV-VIS; EPR; therm; elec; elem anal	144, 214
$Cu(R–R'Hpox)_2$ R = 4-OH; R′ = Bu	Yellow-white	KBr: 3500	KBr: 1600	sp (*trans*)	Elem anal; UV-VIS; elec; IR; tit; graph; grav	178, 211
$Cu(R–R'Hpox)_2$ R = 5-C_8H_{17} R′ = C_8H_{17}	–	KBr: 2931	KBr: 1634	sp or tet	UV-VIS; graph; PMR; IR	69
$Cu(R–R'Hpox)_2$ R = 4-$C_8H_{17}O$ R′ = C_8H_{17}	–	KBr: 2942	KBr: 1631	sp or tet	UV-VIS; graph PMR; IR	69
Zinc(II)						
$Zn(R'Hpox)^+$ R′ = Me	–	–	–	–	Tit	162
Zn(R–R′Hpox) R = H, 3-Me, 4-OH, 4-MeO, 5-Me R′ = Me	White	–	–	–	Tit	144, 162, 164
$Zn(X–R'Hpox)_2$ X = 3-Cl, Br, 5-Cl, Br, I, NO_2; R′ = Me	White	–	–	–	Tit	162
$Zn(R–R'Hpox)_2$	White	–	–	–	Tit	144, 162

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
R = 5-Me, R′ = Me, Et, Pr						144, 162
$Zn(Y–R'Hpox)_2$ Y = 5-NO_2; R′ = Et	White	–	–	–	Tit	188
Niobium(V)						
[Nb–(R–R′Hpox)]—yellow complex reported (probably $NbO(OH)(R–R'Hpox)_2$) R = 4-OH; R′ = Me					Grav	130
Molybdenum(VI)						
$MoO_2(R–R'Hpox)_2$ R = 5-OH; R′ = Me	Orange-yellow	–	–	–	UV-VIS; tit; graph; grav	219
$MoO_2(X,X'–R'Hpox)_2$ X = 3-Cl; X′ = 5-Cl R′ = Me	Orange-yellow	–	–	–	UV-VIS; tit; graph	220
$MoO_2(R–R'Hpox)_2$ R = 5-C_9H_{19}; R′ = C_4H_9	–	–	–	–	Graph	70
$MoO_2(R–R'Hpox)_2$ R = 5-C_9H_{19}; R′ = C_5H_{11}	–	–	–	–	Graph	70
$MoO_2(R–R'Hpox)_2$ R = 5-Me; R′ = C_6H_{13}	–	3280–3170	1575	–	IR; graph	70
Palladium(II)						
$Pd(R'Hpox)_2$ R′ = Me	Yellow-green	3260	1545	sp (*trans*)	Elem anal; mag; tit; IR	151, 194, 221, 222, 274
$Pd(R–R'Hpox)_2$ R = 4-OH; R′ = Me	Yellow	–	–	–	Elem anal; UV-VIS; graph; therm	199, 223, 224
$Pd(R–R'Hpox)_2$ R = 4-Me; R′ = Me	Yellow	–	–	sp	Elem anal; mag; MW; tit; elec; graph; grav	225
$Pd(R–R'Hpox)_2$ R = 4-MeO; R′ = Me	Yellow	–	–	sp	Tit	164

$Pd(R–R'Hpox)_2$ R = 5-Me; R' = Me	Yellow	3260	1545	sp (*trans*)	MW; mag; tit; elem anal; IR	144, 274
$Pd(R,R''–R'Hpox)_2$ R = 3-Me; R'' = 5-Me R' = Me	Yellow	–	–	–	UV-VIS; elem anal	226
$Pd(X,X'–R'Hpox)_2$ X = 3-Cl; X' = 5-Cl R' = Me	Yellow	2850	1560	sp	Elem anal; UV-VIS; IR; tit	227
$Pd(R–R'Hpox)_2$ R = 4-Me; R' = Et	Yellow	–	–	–	Elem anal; IR	228
$Pd(R–R'Hpox)_2$ R = 5-Me; R' = Et	Yellow	–	–	sp (*trans*)	Elem anal; UV-VIS; tit; graph; therm; MW; mag; grav	144, 159, 160, 209, 229
$Pd(R–R'Hpox)_2$ R = 5-Me; R' = Pr	Yellow	–	–	sp (*trans*)	MW; mag; tit	144
$Pd(R–R'Hpox)_2$ R = 4-OH; R' = Bu	Yellow	3280	1590	sp	Elem anal; UV-VIS; IR; graph; tit; grav	230
Uranium(VI)						
$UO_2(R'Hpox)_2$ R' = Me	Orange-yellow	–	–	oct (*trans*)	Elem anal; mag; UV-VIS; tit	151, 231, 232
$UO_2(R–R'Hpox)_2$ R = 3-Me, 4-OH, 4-MeO, 5-Me; R' = Me	Orange-yellow	–	–	–	Tit	164, 231
$UO_2(X–R'Hpox)_2$ X = 3-Cl, Br, 5-Br, I, NO_2; R' = Me	Orange-yellow	–	–	–	Tit	231
$UO_2(X–R'Hpox)$ X = 5-Cl; R' = Me	Orange-yellow	–	–	–	Elem anal; tit; UV-VIS	231, 233
$UO_2(X,X'–R'Hpox)_2$ X = 3-Cl; X' = 5-Cl; R' = Me	Orange-yellow	–	–	–	UV-VIS; tit; graph	220
$UO_2(R,X–R'Hpox)_2$ R = 4-Me; X = 5-Cl; R' = Et	Yellow	–	–	oct	Elem anal; mag	150

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
2-Hydroxy-benzophenone oximes (H_2bpox)						
Nickel(II)						
$Ni(R-Hbpox)_2$ $R = 5\text{-}C_9H_{19}$	Green	KBr: 2950 s br	KBr: 1545 m	sp	UV-VIS; tit; elem anal; MW; IR; graph; mag; PMR	39, 65, 71, 233, 234
$Ni(R-Hbpox)_2$ $R = 5\text{-}C_{12}H_{25}$	Green	–	–	sp (*trans*)	UV-VIS	235
$Ni(X,R-Hbpox)_2$ $X = 3\text{-}Cl$; $R = 5\text{-}C_9H_{19}$	Green	–	–	sp	UV-VIS; elem anal; IR	65, 234
Copper(II)						
$Cu(R-Hbpox)_2$ $R = 5\text{-}C_8H_{17}$	–	KBr: 3028	KBr: 1629	sp or tet	UV-VIS; graph; IR; PMR	69
$Cu(R-Hbpox)_2$ $R = 5\text{-}C_9H_{19}$	Green	KBr: 3000 s br	KBr: 1545 m	sp (*trans*)	UV-VIS; tit; mass; IR; PMR; graph; mag; MW	23, 65, 71, 72, 73, 233, 234, 255
$[Cu(R-Hbpox)]_2^{2+}$ $R = 5\text{-}C_9H_{19}$	Green	–	–	sp	UV-VIS	23
$Cu(R-Hbpox)_2$ $R = 5\text{-}C_{12}H_{25}$	–	–	–	–	Graph	75
$Cu(X,R-Hbpox)_2$ $X = 3\text{-}Cl$; $R = 5\text{-}Me$	Green	–	–	–	UV-VIS; grav; mag	277
$Cu(X,R-Hbpox)_2$ $X = 3\text{-}Cl$; $R = 5\text{-}C_9H_{19}$	–	–	–	–	UV-VIS; IR; graph	65, 74
$Cu(R-Hbpox)_2$ $R = 3\text{-}C_8H_{17}O$	–	–	–	–	IR	76
$Cu(R-Hbpox)_2$ $R = 4\text{-}C_8H_{17}O$	–	KBr: 303?	KBr: 1624	sp or tet	IR; UV-VIS; graph; PMR	69, 76

2-Hydroxy-chalcone oximes (H_2cox)$_2$

Iron(II)						
$Fe(R,R'-Hcox)_2 \cdot 5\ H_2O$ R = 4′-MeO; R′ = 5-Me	Violet	2880 br	1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm	236
$Fe(X,R,R'-Hcox)_2 \cdot 4\ H_2O$ X = 3-Br; R = 4′-MeO; R′ = 5-Me	Violet	Nujol: 2900 s br	Nujol: 1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm	313
Iron(III)						
$Fe(R,R'-Hcox)_3 \cdot 6\ H_2O$ R = 4′-MeO; R′ = 5-Me	Violet	2900 m br	1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm	236
$Fe(X,R,R'-Hcox)_3 \cdot 5\ H_2O$ X = 3-Br; R = 4′-MeO; R′ = 5-Me	Violet	Nujol: 2900 m br	Nujol: 1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm	313
Cobalt(II)						
$Co(R,R'-Hcox)_2$ R = 4′-MeO; R′ = 5-Me	–	–	–	–	UV-VIS	77
$Co(R,R'-Hcox)_2 \cdot 3\ H_2O$ R = 4′-MeO, R′ = 5-Me	White-yellow	2870 m br	1590 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm	236
$Co(X,R,R'-Hcox)_2 \cdot 3\ H_2O$ X = 3-Br; R = 4′-MeO; R′ = 5-Me	Green	Nujol: 2900 m br	Nujol: 1600 m	oct	Elem anal; IR; mag; UV-VIS; elec; therm	313
Nickel(II)						
$Ni(R,R'-Hcox)_2 \cdot 2\ H_2O$ R = 4′-MeO; R′ = 5-Me	Green	2900 m br	1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm; grav	236, 237
$Ni(X,R,R'-Hcox)_2 \cdot 2\ H_2O$ X = 3-Br; R = 4′-MeO; R′ = 5-Me	Yellow	Nujol: 2900 w br	Nujol: 1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm; grav	313
Copper(II)						
$Cu(R,R'-Hcox)_2 \cdot 3\ H_2O$ R = 4′-MeO; R′ = 5-Me	Yellow-brown	2900 m br	1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm; tit; graph; grav	236–239
$Cu(X,R,R'-Hcox)_2 \cdot 3\ H_2O$ X = 3-Br; R = 4′-MeO; R′ = 5-Me	Yellow	Nujol: 2900 w br	Nujol: 1600 s	oct	Elem anal; IR; mag; UV-VIS; elec; therm; tit; graph	239, 313

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
Palladium(II)						
$Pd(R,R'-Hcox)_2$ R = 4′-MeO; R′ = 5-Me	Orange-yellow	2900	1600	sp	Elem anal; IR; mag; UV-VIS; elec; therm; tit; graph; grav	236, 237, 240, 241
$Pd(X,R,R'-Hcox)_2$ X = 3-Br; R = 4′-MeO; R′ = 5-Me	Orange-yellow	Nujol: 2900 w br	Nujol: 1600 s m	sp	Elem anal; IR; mag; UV-VIS; elec; therm; tit; graph	240, 241, 313
Uranium(VI)						
$UO_2(R,R'-Hcox)_2$ R = 2′-OH; R′ = H, 3-Me, 4-Me, 5-Me	Yellow-brown	Nujol: 3400 br m	Nujol: 1545 m	oct (*trans*)	Elem anal; IR; grav; elec	242
$UO_2(R,X-Hcox)_2$ R = 2′-OH; X = 5-Cl	Yellow-brown	Nujol: 3400 br m	Nujol: 1540 m	oct (*trans*)	Elem anal; IR; elec; grav	242
2-Hydroxy-1-naphthaldoximes (H_2nox)						
Titanium(IV)						
$[TiO(OH)(Hnox)]_2$	Orange-red	Nujol: 3340 br	Nujol: 1518	dimeric	Elem anal; IR; elec; MW; mag; therm; grav	242
$TiO(Hnox)_2$	Orange-red	Nujol: 3320	Nujol: 1618	tbp	Elem anal; IR; PMR; elec; MW	48
Vanadium(IV)						
$VO(Hnox)_2$	Brown	Nujol: 3260–3180	Nujol: 1550	spy (*trans*)	Elem anal; IR; UV-VIS; mag; elec	51, 243
Zinc(II)						
Zn(nox)	Yellow	–	–	–	Graph	244
Niobium(V)						
[Nb–(Hnox)]—yellow complex reported (probably $NbO(OH)(Hnox)_2$)					Grav	130

Palladium(II)						
$Pd(Hnox)_2$	Yellow	3245	1543	sp	Elem anal; IR; EPR; therm; UV-VIS; grav	245, 246
Uranium(VI)						
$UO_2(Hnox)_2$	Yellow-brown	Nujol: 3200 br m	Nujol: 1535	oct	Elem anal; IR; elec	139
2-Hydroxy-1-alkylnaphthone oximes ($H_2R'nox$)						
Copper(II)						
$Cu(HR'nox)_2$ R′ = Me	Brown	–	–	–	Elem anal; grav	247
1-Hydroxy-2-alkylnaphthone oximes (H_2Rnox)						
Manganese(II)						
$Mn(HRnox)_2$ R = Et	Green	–	–	–	Elem anal; grav	248
Nickel(II)						
$Ni(HRnox)_2$ R = Me	Yellow-green	–	–	–	Grav	249
Copper(II)						
$Cu(HRnox)_2$ R = Me	Gray	–	–	–	Grav	249
$Cu(HRnox)_2$ R = Et	Yellow-white	–	–	–	Elem anal; therm; grav	250
Palladium(II)						
$Pd(HRnox)_2$ R = Me	Yellow	–	–	–	Grav	249
$Pd(HRnox)_2$ R = Et	Yellow	–	–	–	Elem anal; grav	251
3-Hydroxy-2-alkylnaphthone oximes ($H_2R''nox$)						
Copper(II)						
$Cu(HR''nox)_2$ R″ = Me	Yellow-brown	–	–	–	Grav	252

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Refer-ence(s)
8-Hydroxy-1-tetralone oximes (H_2tox)						
Nickel(II)						
$Ni(R–Htox)_2$	Green	–	–	–	–	253
R = 5-MeO						
Copper(II)						
$Cu(R–Htox)_2$	Yellow	–	–	–	–	253
R = 5-MeO						
2-Hydroxy-1,4-naphthoquinone monoximes (H_2nqox)						
Nickel(II)						
$Ni(Hnqox)_2$	–	–	–	–	Grav	254
Palladium(II)						
$Pd(Hnqox)_2$	–	–	–	–	Grav	254
3-Hydroxy-2-alkyl-1,4-naphthoquinone monoxime (H_2Rnqox)						
Iron(III)						
$[Fe(H_2Rnqox)_2]^{3+}$	Brown	–	–	–	UV-VIS; grav; elem anal;	78
R = Me					graph	
Nickel(II)						
$[Ni(H_2Rnqox)_3]^{2+}$	Red	–	–	–	UV-VIS; graph	79
R = Me						
Ruthenium(III)						
$[Ru(H_2Rnqox)_2]^{3+}$	–	–	–	–	UV-VIS; graph	80
R = Me						
Osmium(VIII)						
$OsO_4(H_2Rnqox)_2$	–	–	–	–	UV-VIS; graph	80

Acyloin oximes ($R,R-H_2ox$); R = alkyl; R′ = aryl

Titanium(IV) $[Ti(R',R'-ox)_2]_2$ R′ = Ph	Yellow	Absent	1670	dimeric	Elem anal; IR; MW; PMR	278
Vanadium(V) $VO_2(R',R'-Hox)$ R′ = Ph	White	–	–	–	Elem anal; graph; grav	257
Iron(III) $Fe(R,R-Hox)_3$ R = PrCH(Me), C_5H_{11}, BuCH(Me)	–	–	–	–	Graph	24
Cobalt(II) $Co(R,R-Hox)_2$ R = BuCH(Et)	Brown	–	–	–	UV-VIS; graph	81
$Co(R,R-H_2ox)_3Y_2$ R = BuCH(Et), Y = HDNNS	–	–	–	–	Graph	33, 35, 45
Cobalt(III) $[Co(R,R-Hox)_2(R,R-H_2ox)]^+$ R = BuCH(Et)	Green	–	–	–	UV-VIS; graph	81
Nickel(II) $[Ni(R,R-Hox)(R,R-H_2ox)_2]^+$ R = BuCH(Et)	Blue	–	–	–	UV-VIS; graph	81
$[Ni(R,R-ox)]_n$ R = BuCH(Et)	Olive	Absent	1580 m	oligomeric	Elem anal; MW; mass; UV-VIS; therm; mag; IR; PMR; X-ray	71, 82, 83
$Ni(R,R-Hox)_2$ R = Pr, PrCH(Me), C_5H_{11}	–	–	–	–	Graph	24
$Ni(R,R-Hox)_2$ R = BuCH(Et)	Orange-red	–	–	sp	UV-VIS; graph; IR; PMR; mass; elem anal; X-ray; mag; MW; therm	24, 37, 71, 81–84
$Ni(R,R-Hox)_2(R,R-H_2ox)$ R = BuCH(Et)	Blue	–	–	–	UV-VIS; mass; tit; IR	39, 71, 82, 85

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
$Ni(R,R\text{–}Hox)_2(H_2O)_2$ R = BuCH(Et)	–	–	–	oct	UV-VIS	71
$Ni(R,R\text{–}H_2ox)_3X_2$ R = BuCH(Et), X = SO_4	Blue	KBr: 2900 s br 3600 sh	KBr; 1645 br	oct	Elem anal; MW; grav; IR; therm; PMR; X-ray; mass; mag; tit	71, 82, 83, 85
$Ni(R',R'\text{–}Hox)_2$ R' = C_4H_3O	Green-yellow	–	–	–	Elem anal; mag	258
$Ni(R',R'\text{–}H_2ox)_2X_2$ R' = C_4H_3O; X = Cl, NO_3	–	–	–	oct	IR; UV-VIS; X-ray; mag; therm	259
$Ni(R,R\text{–}Hox)_2Y_2$ R = BuCH(ET); Y = LA	Green	–	–	–	Graph; UV-VIS	37
$Ni(R,R\text{–}H_2ox)_3Y_2$ R = BuCH(Et); Y = VSA	–	–	–	–	IR; mass	39
$Ni(R,R\text{–}H_2ox)_3Y_2$ R = BuCH(Et); Y = HDNNS	–	–	–	–	Graph; UV-VIS	33, 35, 42, 43, 45
$K[NiH(R',R'\text{–}ox)_2]$ R' = Ph	Red	–	–	sp (*trans*)	Elem anal; mag	258
$Ni(R',R'\text{–}Hox)_2$ R' = Ph	Yellow-green	–	–	–	Elem anal; mag; MW	258, 260, 261
$Ni(R',R'\text{–}H_2ox)X_2$ R' = Ph; X = Cl, Br, I, NO_3, ClO_4, SCN, OAc	–	–	–	oct	Elem anal; mag; IR; UV-VIS; X-ray; therm	280
$Ni(R',R'\text{–}H_2ox)_2Y_2\cdot 2\ H_2O$ R' = Ph; Y = $MeCO_2$	Green	–	–	oct (*trans*)	Elem anal	260
$K[NiH(R,R'\text{–}ox)_2]$ R' = $C_7H_5O_2$	Red	–	–	sp (*trans*)	Elem anal; mag	258
$Ni(R',R'\text{–}Hox)_2$ R' = $C_7H_5O_2$	Yellow-green	–	–	–	Elem anal; mag	258
$K[NiH(R',R'\text{–}ox)_2]$ R' = C_7H_7O	Red	–	–	sp (*trans*)	Elem anal; mag	258

$Ni(R',R'-Hox)_2$ $R' = C_7H_7O$	Yellow-green	–	–	–	Elem anal; mag	258
$Ni(R',R'-H_2ox)_2X_2$ $R' = C_7H_7O$; $X = Cl, NO_3$	–	–	–	oct	IR; UV-VIS; X-ray; mag; therm	259
$Ni(R',R'-H_2ox)_2X_2$ $R' = C_8H_{10}N$; $X = Cl, NO_3$	–	–	–	oct	IR; UV-VIS; X-ray; mag; therm	259
Copper(II)						
$[Cu(R,R-ox)]_n$ $R = Me, C_4H_3O$	Green	–	–	polymeric	Elem anal; mag	262
$[Cu(R,R-ox)]_n$ R = Pr, t-Bu, PrCH(Me), C_5H_{11}, MeCH(Me)Et	Green	–	–	polymeric	Graph	24
$[Cu(R,R-ox)]_n$ R = Bu	Green	–	–	planar polymeric	Elem anal; mag; graph	24, 262
$Cu(R,R-Hox)_2$ R = BuCH(Et)	Blue-green	Absent	–	sp (*trans*)	Graph; PMR; IR; chrom; mag; MW	24, 263, 264
$[Cu(R,R-ox)]_n$ R = BuCH(Et)	Green	Absent	KBr: 1590 m	oligomeric	Graph; PMR; IR; chrom; elem anal; mag; mass; X-ray; MW; therm; tit	24, 71, 83, 85, 263, 264
$[Cu(R,R-ox)]_n$ $R = C_9H_{19}$	Green	Absent	–	polymeric	IR; PMR; chrom	263, 264
$Cu(R,R-H_2ox)_3X$ R = BuCH(Et); $X = SO_4$	Blue	KBr: 3000 s br 3600 sh	KBr: 1645 br	oct	IR; PMR; UV-VIS; mass; elem anal; mag; X-ray; MW; therm	71, 83
$Cu(R,R-Hox)_2Y_4$ R = BuCH(Et); Y = ABLA	–	–	–	–	UV-VIS; graph	41
$[Cu(R,R'-ox)]_n$ R = H, $(Me)_2(Me)Ph$ R' = Ph	Green	–	–	polymeric	Sol; grav	265
$[Cu(R',R'-ox)]_n$ $R' = C_4H_3O$	Green	–	–	polymeric	Elem anal; mag; sol	262, 265
$[Cu(R',R'-ox)]_n$ $R' = C_4H_3S$	Green	–	–	polymeric	Sol; grav	275

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
$[Cu(R',R'-ox)]_n$ R' = Ph	Green	–	–	polymeric	Elem anal; mag; EPR; tit; therm	2, 4, 115, 116, 119, 121, 260–262, 265–268
$[Cu(R',R'-H_2ox)_2X_2]$ R' = Ph; X = Cl	Green-blue	–	–	sp	Elem anal; mag	260, 262
$[Cu(R',R''-ox)]_n$ R' = Ph; R'' = $(Ph)_2$	Green	–	–	polymeric	Sol	265
Yttrium(III)						
$Y(R',R-H_2ox)_3X_3$ R' = Ph; X = Cl	–	KBr: 3260 s	KBr: 1626 m	–	Elem anal; X-ray; IR; therm	276
$Y(R',R'-Hox)X_2 \cdot 2\ H_2O$ R' = Ph; X = Cl	–	Nujol: 3250	Nujol: 1650	–	Elem anal; UV-VIS; IR	179
Niobium(V)						
$Nb(R',R'-ox)Y_3$ R' = Ph; Y = EtO	Yellow	–	Nujol: 1635	oligomeric	Elem anal; IR; MW	275
$Nb(R',R'-ox)_2Y$ R' = Ph; Y = EtO	–	–	Nujol: 1635	oligomeric	Elem anal; IR; MW	275
$NbH(R',R'-ox)_3$ R' = Ph	Red	–	Nujol: 1635	oligomeric	Elem anal; IR; MW	275
Molybdenum(VI)						
$MoO_2(R,R-Hox)_2$ R = BuCH(Et)	–	–	–	oct (*trans*)	Chrom	263
$MoO_2(R,R-Hox)_2$ R = C_9H_{19}	–	–	–	oct (*trans*)	PMR; IR; chrom	263
$MoO_2(R',R'-Hox)_2$ R' = Ph	White	–	–	–	Elem anal; therm; grav; graph	115, 257, 269, 270, 312

Rhodium(I)						
$Rh(R',R'–Hox)_2(CO)_2$ $R' = Ph$	Brown	–	–	–	Elem anal; MW; IR; elec	281
Palladium(II)						
$Pd(R',R'–Hox)_2$ $R' = Ph$	Yellow	–	–	–	Elem anal; MW; UV-VIS	260, 271
Lanthanum(III)						
$La(R',R'–H_2ox)_3X_3$ $R' = Ph$; $X = Cl$	–	KBr: 3260	KBr: 1626	–	Elem anal; IR; X-ray; therm	276
$La(R',R'–Hox)_2X \cdot 2\ H_2O$ $R' = Ph$; $X = Cl$	–	Nujol: 3250	Nujol: 1620 br	–	Elem anal; IR; UV-VIS	179
Cerium(IV)						
$Ce(R',R'–H_2ox)_3X_3$ $R' = Ph$; $X = Cl$	–	KBr: 3200 s	KBr: 1624 m	–	Elem anal; IR; X-ray; therm	276
$Ce(R',R'–Hox)_2X \cdot 2\ H_2O$ $R' = Ph$; $X = Cl$	–	Nujol: 3250	Nujol: 1610 br	–	Elem anal; IR; UV-VIS	179
Praseodymium(III)						
$Pr(R',R'–H_2ox)_3X_3$ $R' = Ph$; $X = Cl$	–	KBr: 3240 s	KBr: 1620 m	–	Elem anal; IR; X-ray; therm	276
$Pr(R',R'–Hox)_2X$ $R' = Ph$; $X = Cl$	Yellow	Nujol: 3400–3300 br	Nujol: 1650	–	Elem anal; IR; UV-VIS; therm	272
Neodymium(III)						
$Nd(R',R'–H_2ox)_3X_3$ $R' = Ph$; $X = Cl$	–	KBr: 3260 s	KBr: 1622 m	–	Elem anal; IR; X-ray; therm	276
$Nd(R',R'–Hox)_2X$ $R' = Ph$; $X = Cl$	Pink	Nujol: 3400–3300 br	Nujol: 1650	–	Elem anal; IR; UV-VIS; therm	272
Samarium(III)						
$Sm(R',R'–H_2ox)_3X_3$ $R' = Ph$; $X = Cl$	–	KBr: 3240 s	KBr: 1624 m	–	Elem anal; IR; X-ray; therm	276
$Sm(R',R'–Hox)_2X$ $R' = Ph$, $X = Cl$	White	Nujol: 3400–3300 br	Nujol: 1650	–	Elem anal; IR; UV-VIS	272

TABLE 1 (continued)

Compound [a]	Color	ν_{OH} [b]	$\nu_{C=N}$ [b]	Proposed [c] structure	Available [d] analytical data	Reference(s)
Europium(III)						
$Eu(R',R'-H_2ox)_3X_3$	–	KBr:	KBr:	–	Elem anal; IR; X-ray;	276
$R' = Ph$; $X = Cl$		3230	1633 m		therm	
Gadolinium(III)						
$Gd(R',R'-H_2ox)_3X_3$	–	KBr:	KBr:	–	Elem anal; IR; X-ray;	276
$R' = Ph$; $X = Cl$		3255 s	1628 m		therm	
$Gd(R',R'-Hox)_2X$	–	Nujol:	Nujol:	–	Elem anal; IR; UV-VIS	272
$R' = Ph$; $X = Cl$		3200	1625			
Terbium(III)						
$Tb(R',R'-H_2ox)_3X_3$	–	KBr:	KBr:	–	Elem anal; IR; X-ray;	276
$R' = Ph$; $X = Cl$		3238 s	1626 m		therm	
Dysprosium(III)						
$Dy(R',R'-H_2ox)_3X_3$	–	KBr:	KBr:	–	Elem anal; IR; X-ray;	276
$R' = Ph$; $X = Cl$		3260 s	1632 m		therm	
Holmium(III)						
$Ho(R',R'-H_2ox)_3X_3$	–	KBr:	KBr:	–	Elem anal; IR; X-ray;	276
$R' = Ph$; $X = Cl$		3217 s	1624 m		therm	

Erbium(III)						
$Er(R',R'-H_2ox)_3X_3$ $R' = Ph$; $X = Cl$	–	KBr: 3220 s	KBr: 1626 m	–	Elem anal; IR; X-ray; therm	276
Tungsten(VI)						
$WO_2(R',R'-Hox)_2$ $R' = Ph$	–	–	–	oct	Elem anal; IR; grav; therm; graph	115, 257, 273
Platinum(II)						
$Pt(R',R'-Hox)_2$ $R' = Ph$	Yellow	–	–	–	Elem anal; MW; UV-VIS	260, 271

[a] Me = CH_3; Et = C_2H_5; Pr = C_3H_7; Bu = C_4H_9; Ph = C_6H_5; HDNNS = dinonylnaphthalene sulphonic acid; LA = lauric acid [$CH_3(CH_2)_{10}COOH$]; ABLA = α-bromolauric acid [$CH_3(CH_2)_9CH(Br)COOH$]; VSA = Versatic 911 (versatic acid, Shell Chemical Co.).

[b] HCB = hexachlorobutadiene; m = medium; br = broad; s = strong; v = very; w = weak; sh = sharp.

[c] tbp = trigonal bipyramidal; sp = square planar; spy = square pyramidal; oct = octahedral; tet = tetrahedral.

[d] UV-VIS = electronic absorption spectral data; IR = infrared data other than ν_{OH} and ν_{CN}; EPR = electron paramagnetic resonance data; PMR = proton magnetic resonance data; Möss = Mössbauer spectral data; mass = mass spectral data; MW = molecular weight measurements; Elem anal = elemental analysis; mag = magnetic susceptibility data; grav = gravimetric analysis; elec = electrical conductance data; X-ray = X-ray analysis (single crystal or powder diffraction); chrom = chromatographic analysis; sol = solubility data; therm = thermal analyses; tit = titrimetric analyses (potentiometric, amperometric etc.); graph = graphical analyses (continuous variation, slope ratio, mole ratio, etc.).

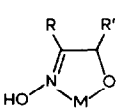
nickel(II) ($Ni(Hbox)_2$) appears before bis-(2-hydroxy-5-chlorobenzaldoximato) nickel(II) ($Ni(X-Hbox)_2$; X = 5-Cl) while both of these complexes are listed before bis-(2-hydroxy-benzaldoximato) copper(II) ($Cu(Hbox)_2$).

Some interesting statistics are revealed in Table 1. Of the 453 complexes listed, the first row transition metals account for about 76% of the entries while nickel (100 entries) and copper (74 entries) together comprise about 38% of the reported transition metal–hydroxyoxime complexes. The ranking by element with respect to the number of entries is as follows: Ni(100) > Cu(74) > Fe(39) > Co(34) > V(31) > U(25) > Zn(24), Pd(24) > Ti(21) > Mn(20) > Mo(10) > Nb(6) > Y(4), La(4), Ce(4), Pr(4), Nd(4), Sm(4), Gd(4) > Pt(3) > Rh(2) > Zr(1), Hf(1), Eu(1), Tb(1), Dy(1), Ru(1), Cd(1), Ho(1), Er(1), W(1), Os(1). The largest class of hydroxyoxime–metal complexes is found to be the 2-hydroxy-alkylphenone oximes with 185 listed compounds followed by the 2-hydroxy-benzaldoximes (salicylaldoximes) with 125 entries. These two classes represent about 68% of the reported transition metal complexes with hydroxyoxime ligands.

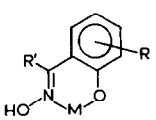
Before discussing the methods used to characterize the reported transition metal–hydroxyoxime complexes, it might be useful to mention briefly some of the fundamental chemical aspects of the hydroxyoxime ligands themselves, in order to clarify the relationship between the ligand properties and the metal complex structure.

B. LIGAND BONDING IN COMPLEXES

Hydroxyoximes are ambidentate with the potential of a variety of coordinate modes depending upon a number of stabilizing factors including steric hindrance, hydrogen bonding and electronic considerations. In a vast majority of the complexes reported, the oximes function as bidentate chelating ligands by bonding through the nitrogen and the oxygen of the phenolic group, as shown in (**V**) and (**VI**) for the acyloin and aromatic *ortho*-hydroxyoximes, respectively.

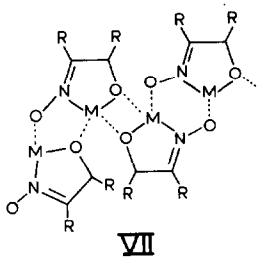


V



VI

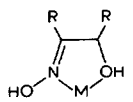
Many of the acyloin oxime complexes with transition metals are reported to involve extensive polymerization with the hydroxyoxime functioning as a dibasic ligand as shown in (**VII**) [24,262–275]. The metal is coordinately saturated as a result of the interaction of the metal with neighboring hydroxyoxime groups. The strong polymerization is evident by the general



VII

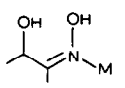
insolubility of many transition metal–acyloin oxime complexes in most common organic solvents [265] and by the anomalously low magnetic moments ascribed to antiferro-magnetic interactions [83,262].

The acyloin oximes also have been reported to act as neutral bidentate ligands with transition metals [83,260] in which the hydroxyoxime is coordinated with both the hydroxyl and oxime groups protonated (**VIII**). This coordination mode usually occurs only under acidic conditions.

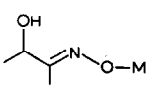


VIII

In addition to hydroxyoxime ligands functioning by a bidentate chelation mechanism, they may also coordinate to transition metals by a monodentate mechanism through the nitrogen (**IX**) or oxygen (**X**) of the oxime group. Although no transition-metal complexes of type (**X**) have been reported, there is convincing evidence of type (**IX**) bonding in a number of complexes [276].



IX



X

More detailed analyses of the bonding in many of the transition metal hydroxyoxime complexes can be found under the Methods of Characterization sections.

C. COMPLEX SYNTHESIS

Examination of the methods used to synthesize the transition metal–hydroxyoxime complexes listed in Table 1 reveals that the majority have been

prepared via three general types of reaction: (1) conventional precipitation, (2) homogeneous precipitation and (3) solvent extraction. Each of these synthetic methods is discussed below and several examples are given in each case.

(i) Conventional precipitation

Conventional precipitation is the most commonly used synthetic method for the preparation of transition metal complexes with hydroxyoximes. It involves the direct contact of a transition metal salt with the hydroxyoxime ligand in aqueous solution under appropriate pH conditions. Typically, an ethanolic solution of the hydroxyoxime ligand is added to a stirred aqueous solution of the metal salt. The reaction solution pH is adjusted as required using an acid or base, the proper temperature is achieved and the resulting precipitate is filtered, washed thoroughly with water and ethanol and dried in air or under vacuum. Typical examples are illustrated in eqns. (1–5).

$$TiO(ClO_4)_2 + [H_2box] \xrightarrow[RT]{H_2O} TiO(Hbox)_2 \quad (1)\ [48]$$

$$VOCl_2 + [H_2nox] \xrightarrow[Reflux]{EtOH} VO(Hnox)_2 \quad (2)\ [51]$$

$$Co(NO_3)_2 + [H_2box] \xrightarrow[RT;\ pH\ 8]{H_2O/EtOH} Na[CoH(box)_2] \quad (3)\ [55]$$

$$(NH_4)VO_3 + [R'H_2box] \xrightarrow[RT;\ pH\ 3]{H_2O/EtOH} VO(OH)(R'Hbox)_2 \quad (4)\ [151]$$

$$LaCl_3 + [R',\ R\text{–}H_2ox] \xrightarrow[RT;\ pH\ 6.5]{EtOH} [La(R',\ R'\text{–}H_2ox)_3Cl_3] \quad (5)\ [276]$$

The complexes generally are air and thermally stable while product yields are quantitative, making many of the hydroxyoximes excellent analytical reagents for gravimetric analysis of metal ions in solution. However, one disadvantage of the conventional precipitation method is that for certain hydroxyoxime complexes, notably the salicylaldoximes, the precipitates are often gelatinous, making them difficult to filter and wash [102,282]. For these complexes other synthetic methods are often employed.

(ii) Homogeneous precipitation

Preparation of transition metal complexes by the method of precipitation from homogeneous solution (PFHS) was first introduced by Bickerdike and Willard [284] and later was more fully developed by Gordon and co-workers [285]. Basically, the process involves generating the reactant ligand in situ in

the presence of the metal with which the ligand is to complex. This preparative method can be quite superior to conventional precipitation for certain oxime complexes. The precipitates obtained by the homogeneous process are often of higher purity and more easily filterable [283,286] than those produced from the conventional precipitation method.

Pietrzak and Gordon [282] were the first workers to use the PFHS method for the preparation of transition metal–hydroxyoxime complexes. They synthesized salicylaldoxime (H_2box) from salicylaldehyde (H_2ba) and hydroxylamine hydrochloride in the presence of Cu(II) to precipitate $Cu(Hbox)_2$ (see eqn. 6). Relatively few hydroxyoxime complexes have been prepared by PFHS techniques and some of the examples are reported as illustrated in eqns. (6–9).

$$CuSO_4 + [H_2ba] + NH_2OH \cdot HCl \xrightarrow[5°C;\ pH\ 2.9]{H_2O} Cu(Hbox)_2 \qquad (6)\ [282]$$

$$Ni(NO_3)_2 + [H_2ba] + NH_2OH \cdot HCl \xrightarrow[RT;\ pH\ 10]{EtOH/H_2O} Ni(Hbox)_2 \qquad (7)\ [102]$$

$$PdCl_2 + [H_2ba] + NH_2OH \cdot HCl \xrightarrow[RT;\ 2\%\ H_2SO_4]{EtOH/H_2O} Pd(Hbox)_2 \qquad (8)\ [102]$$

$$Ni^{2+} + [H_2ba] + NH_2OH \cdot HCl \xrightarrow[RT;\ pH\ 6-7]{H_2O} Ni(Hbox)_2 \qquad (9)\ [283]$$

Although the PFHS method apparently has received little serious consideration as a synthetic method for the preparation of transition metal–hydroxyoxime complexes, one commercial process is utilizing a modified PFHS technique for regeneration of aromatic *ortho*-hydroxyoxime reagents in metallurgical solvent extraction systems [287].

(iii) Solvent extraction

Hydroxyoximes have proven to be useful reagents for the extraction of metal ions from aqueous solution both for analytical purposes and for commercial metallurgical production. Solvent extraction (SX) involves the partitioning of a chemical substance between two immiscible phases as a result of mutual solubility [288,289]. For the extraction of metals from aqueous solution, an organic phase containing a reagent capable of complexing with the metal of interest is used. The process is often described by

$$M^{n+}_{aq} + nRH_{org} \rightleftharpoons (MR_n)_{org} + nH^+_{aq} \qquad (10)$$

where the subscripts aq and org refer to the aqueous and organic phases, respectively.

Although SX with hydroxyoximes has been studied extensively in the context of commercial applications [19–24,25,27,136,290,291], as a synthetic method for the preparation of transition metal–hydroxyoxime complexes, SX has not been used very extensively. Few of the complexes listed in Table 1 were actually isolated using SX methods. However, many of the complexes were characterized by analytical methods in situ following extraction of the metal into an organic phase using hydroxyoxime compounds. A variety of extraction conditions are often used, as illustrated in eqns. (11–14).

$$NiCl_{2\,aq} + [H_2box]_{org} \xrightarrow[pH\ 7.0]{benzene} [Ni(Hbox)_2]_{org} \quad (11)\ [26]$$

$$PdCl_{2\,aq} + [R\text{–}R'H_2pox]_{org} \xrightarrow[pH\ 2]{CCl_4} [Pd(R\text{–}R'Hpox)_2]_{org} \quad (12)\ [229]$$

$$CuSO_{4\,aq} + [H_2ox]_{org} \xrightarrow[pH\ 2.5\text{–}4.5]{toluene} [Cu(ox)_n]_{org} \quad (13)\ [24]$$

$$CuSO_{4\,aq} + [R\text{–}H_2box]_{org} \xrightarrow[pH\ 1.4\text{–}3.2]{ClCH_2CH_2Cl} [Cu(R\text{–}Hbox)_2]_{org} \quad (14)\ [123]$$

Usually an excess of metal salt is used to insure complete complexation of the oxime and the organic phase is washed repeatedly with water to remove entrained aqueous phase. The complex usually can be isolated simply by removing the organic solvent by distillation under reduced pressure.

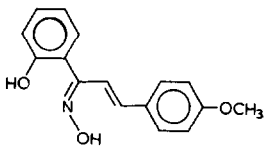
D. METHODS OF CHARACTERIZATION

Several analytical techniques have been used to characterize transition metal–hydroxyoxime complexes. The methods chosen to characterize a particular complex depend upon the nature of that complex as well as the type of information required. For example, soluble complexes which oligomerize in solution are readily characterized by molecular weight measurements and Beer's Law analyses using electronic absorption spectroscopy, whereas these techniques are of little use for characterizing insoluble polymeric complexes. Similarly, if one is interested in the stereochemistry of the complex, the most versatile techniques are IR, NMR, X-ray diffraction and electronic absorption spectroscopy. We cannot, because of space limitation, discuss all the common characterization techniques in detail, but a few of the more important methods are highlighted.

(i) Electronic absorption spectroscopy

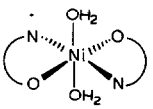
Electronic absorption spectroscopy has been used extensively for characterizing transition metal–hydroxyoxime complexes. The spectra obtained

are characteristic of the structure of the complex and quite often a reasonable structure can be assigned to a complex based on the appearance of the UV-VIS spectrum alone. For example the electronic absorption spectrum of the Ni(II) complex with 2-hydroxy-4′-methoxy-5-methylchalcone oxime (**XIII**) [236] resembles the spectra of other octahedral Ni(II) complexes.



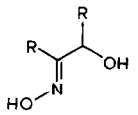
XIII

The octahedral spectra are sufficiently different from the electronic absorption spectra of tetrahedral or square planar Ni(II) complexes [294] that an octahedral structure (**XIV**) was assigned to the complex.



XIV

Similarly, the electronic absorption spectrum of the Ni(II) complex with an aliphatic acyloin oxime (**XV**; R = n-BuCH(Et)) has been reported to be typical of nickel square-planar complexes [37] and the structure assigned accordingly.



XV

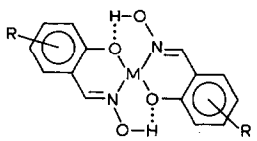
Detailed analyses of the absorption spectra and assignment of the electronic transitions have been accomplished for a number of the complexes listed in Table 1. As an illustration, the electronic absorption spectrum for the Ni(II)–hydroxychalcone oxime previously described has been examined in detail [236] and the three moderately intense bands in the 1000–400 nm region have been assigned to the three spin-allowed transitions of Ni(II) in an octahedral environment of $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. However, in general, the electronic absorption spectra of the transition metal–hydroxyoxime complexes listed in Table 1 have been used for spectrophotometric determination of metal–ligand stability con-

stants and for graphical analyses of the metal complex stoichiometry. These characterization methods are described in more detail in subsequent sections.

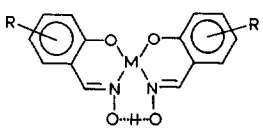
(ii) Infrared spectroscopy

Infrared spectroscopy has been very useful in structure investigations of transition metal–hydroxyoxime complexes. In general, it is not possible to determine the structure or composition of a metal–hydroxyoxime complex by its infrared spectrum alone, although the spectrum can provide several useful indicators. The regions which have proven most helpful for structural analysis are the 3600–2400 cm^{-1} region where hydroxyl stretching modes are found and the 1700–1500 cm^{-1} region where the C = N group generally absorbs (Table 1).

The shapes and positions of the bands assigned to OH vibrations can be utilized to provide information on the nature of the bridging intramolecular hydrogen bonds formed in the transition metal complexes. Burger et al. [54,55] and Ramaswamy et al. [56] have examined the hydrogen bonding in a variety of substituted salicylaldoxime complexes and they have shown that strong hydrogen bridges are formed in all complexes of type (**XI**) (*trans*) or (**XII**) (*cis*) depending upon the metal.



XI



XII

The exact frequency of the OH vibrations is often difficult to ascertain with any precision as a result of very broad bands which are often observed in the transition metal–hydroxyoxime complexes. However, on the basis of the infrared results presented for the complexes listed in Table 1, three types of hydrogen bridge can be distinguished [55,100,293]:

(i) A sharp band of medium to high intensity in the region 3300–2900 cm^{-1} characteristic of a polarized hydrogen bridge.

(ii) A sharp band of medium intensity at about 3450 cm^{-1} which can be attributed to a hydrogen bridge linked through the nitro group.

(iii) A broad band of low intensity in the region 3400–2400 cm^{-1} characteristic of a hydrogen bridge of low polarity.

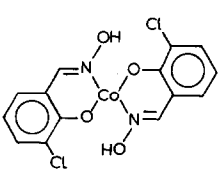
Most of the reported transition metal–hydroxyoxime complexes appear to exhibit the type of hydrogen bridging described by (iii) above, as shown by the ν_{OH} values listed in Table 1. Nucleophilic and electrophilic substitutions in the hydroxyoxime ligand have been shown [55] to have considerable effect

on the position of the OH bands, indicating a stabilizing or destabilizing of the hydrogen bond. The stability order for some common substituents is $CH_3 > H > Cl > NO_2$ which has been interpreted in terms of the electron density on the oxygen atoms linked by the hydrogen bond [55].

The shifting in stretching frequency of the C = N group also has been examined in a number of the metal–hydroxyoxime complexes as a method of investigation of the stability of the metal–ligand bonds. Oximes are known to form both coordinate σ-donor and π-acceptor bonds with transition metals [54,55]. The relative shifting in the C = N stretching can be interpreted in terms of the strength of the σ-donor bond, the π metal → ligand back bonding, and the stability of the intramolecular hydrogen bridging in the transition metal complex. With few exceptions, the frequency of the C = N vibration is shifted to higher wavenumbers as the stability of the complex is increased [55].

(iii) Magnetic susceptibility

Magnetic susceptibility is an extremely useful tool for structural analysis of transition-metal complexes; many hydroxyoxime complexes have been characterized by this technique (Table 1). Magnetic moments determined from molar susceptibility results have been invaluable for examining electronic configuration, bonding mechanisms and ligand field parameters in a number of the complexes. The results have been especially useful for distinguishing unambiguously the structures of many of the Ni(II) high-spin and low-spin complexes. Khanolkar and Khanolkar [180], using magnetic moments derived from susceptibility measurements of halogen substituted 2-hydroxy-acetophenone oxime Co(II) complexes, have proposed that the 3-chloro derivative (**XIX**) represents the high spin–low spin crossover square-planar system.



XIX

Another interesting application of magnetic susceptibility for the structural analysis of hydroxyoxime complexes is in the Cu(II)–acyloin oxime system. The amorphous structure and insolubility in common organic solvents of many of the Cu(II)–acyloin oxime complexes make it difficult to perform any X-ray analyses or molecular weight measurements. However, magnetic susceptibility results clearly show that many of these complexes have subnor-

mal magnetic moments in the range 0.74–0.80 B.M. at room temperature [71,83,262]. These anomalous results have been attributed to anti-ferromagnetic interactions between the copper atoms, indicating polymeric complexes. Structures have been assigned [262] in which each oxygen atom is bridging two copper atoms and coordinate saturation is achieved by interaction of the metal with neighboring hydroxyoxime ligands.

Despite its usefulness for many of the hydroxyoxime–metal complexes, magnetic susceptibility has limitations in its applicability. In many metal systems the differences in magnetic moments among the various structures are small. For example, an observed magnetic moment in the range 1.7–1.8 B.M. for a Cu(II)–hydroxyoxime complex is characteristic of both square-planar and tetragonally distorted symmetry [119] while a value in the range 1.9–2.2 B.M. indicates tetrahedral structure. Unfortunately, room temperature magnetic moments alone often are insufficient to assign a definitive structure to the complex. Therefore, one has to be cautious when using magnetic susceptibility for structural analysis in those systems where structural differences result in only slight variations in the observed magnetic moments.

(iv) Mass spectrometry

Although mass spectrometry is an extremely powerful characterization tool for metal chelate compounds [292], its application to transition metal–hydroxyoxime complexes virtually has been ignored. Only a few of the reported complexes in Table 1 have been examined by mass spectrometry [23,39,66,71,83].

In their analysis of the mass spectrum of 2-hydroxy-5-nonylbenzophenone oxime complex with Cu(II), Pratt and Tilley [23] attributed weak peaks observed at m/z 767 and 753 to the presence of higher homolog impurity ligands. The parent ion (relative intensity = 100) was found at m/z 739. An interesting observation which is reported is the complete gap in the mass spectrum from m/z 650–401, corresponding to complete loss of one ligand.

Keeney and Osseo-Asare [83] in their study on transition-metal complexes of 5,8-diethyl-7-hydroxy-6-dodecanone oxime (R, $R–H_2Ox$, R = n-BuCH(Et)), report that the mass spectra of $[Cu(R, R–Ox)]_n$ and $[Ni(R, R–Ox)]_n$ are nearly identical, suggesting similar structures for the complexes. In addition, the similarity of the mass spectra of $[Cu(R, R–H_2Ox)_3SO_4]$ and $[Ni(R, R–H_2Ox)_3SO_4]$ suggest isostructural symmetry for the complexes.

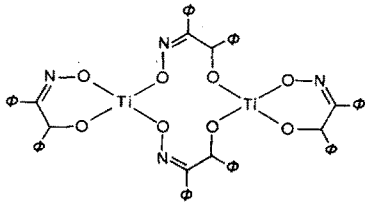
The mass spectral results obtained by Pratt and Tilley [23] and Keeney and Osseo-Asare [83] make it surprising that mass spectrometry has been sparsely used as a method of characterization for transition metal–hydroxyoxime complexes. Application of the technique to other hydroxyoxime

systems should provide the same valuable structural information obtained for other metal chelate complexes in which mass spectrometry is employed.

(v) Nuclear magnetic resonance spectroscopy

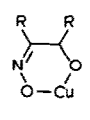
Nuclear magnetic resonance spectroscopy (NMR) is a very powerful analytical technique for the characterization of transition-metal complexes with organic ligands, especially for complexes which exhibit strong hydrogen bridging [295]. ^{1}H NMR (PMR) is capable of giving detailed information on the environment of the hydroxyl protons in the complexes and when combined with infrared data, an excellent picture of the nature of the hydrogen bonds often can be obtained. Unfortunately, as with mass spectrometry, the literature is nearly devoid of NMR characterizations of transition metal–hydroxyoxime complexes. There are no reported ^{13}C, ^{14}N or ^{15}N NMR studies and only few of the listed complexes of Table 1 have been examined by PMR techniques [48,69,71,83,263,264,278].

Biradar and Mahale [48] have examined various substituted salicylaldoxime and naphthaldoxime complexes with Ti(IV) and have shown conclusively that in all cases only the phenolic proton is lost upon coordination of the oxime ligand. However, the α-benzoin oxime complex with Ti(IV) has been shown [278] to lose both the oximic and phenolic protons upon coordination. A novel bonding mechanism (**XVI**) has been proposed for the α-benzoin oxime complex (ϕ = Ph). The structure involves six-member rings in which only Ti–O bonds exist, indicating that the C = N group is not involved directly in coordination.

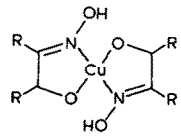


XVI

Fritz et al. [264] have proposed both six-member ring mono-oximato (**XVII**) and five-member ring bis-oximato (**XVIII**) complexes of Cu(II) with [R,R–H_2ox] (R = n-BuCH(Et)) based on PMR data for the hydroxyl and the oximic protons.



XVII



XVIII

However, when a straight chain aliphatic group (C_9H_{19}) is substituted for the branched aliphatic substituent in the acyloin oxime, only structure (**XVII**) is obtained. The Mo(VI) complexes with the same ligands are reported to be of structure (**XVIII**) only [263].

(vi) Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance spectroscopy (EPR) also known as electron spin resonance spectroscopy (ESR), like NMR, has been used to characterize very few of the reported transition metal complexes with hydroxyoxime ligands, as indicated in Table 1. Furthermore, with the exception of a Pd(II) complex of 2-hydroxy-1-naphthaldoxime [245], all the other complexes for which EPR data have been reported are aromatic *ortho*-hydroxyoxime complexes with Cu(II) [121,193,214]. Schoffa et al. [121] have examined the magnetic properties of the Cu(II)–salicylaldoximate and report a g value of 2.095, close to the spin-only value of 2.002. Kapahi et al. [214] report g values in the range 2.11–2.15 for various 2-hydroxy-5-methylalkylphenone oximes with Cu(II) and have assigned complex stabilities based on these results in the order $CH_3 > C_2H_5 > C_3H_7$ for the alkyl substituent. Similarly, Khanolkar and Khanolkar [193] have used EPR for structure studies of various halogen substituted Cu(II) complexes and conclude that the complexes have strong σ and π metal–ligand bonds.

Naidu and Naidu [245] report that the EPR spectra of the 2-hydroxy-1-naphthaldoxime complex with Pd(II) showed that the complex is diamagnetic. They therefore suggested a square-planar structure for the complex.

(vii) X-ray structure determination

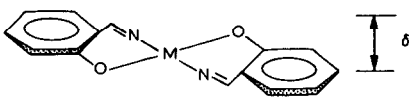
Although no neutron diffraction studies have been performed on transition metal–hydroxyoxime complexes, a few X-ray crystal structures have been reported on transition-metal complexes with salicylaldoxime ligands [101,105,106,117,122,134,135]. The results of the bond length determinations are given in Table 2. In all cases the complexes are *trans*-square planar with strong intermolecular hydrogen bridges. However, the metal atom, oxime nitrogen and oxime oxygen are non-coplanar resulting in a "chair" type structure (**XX**) with a small perpendicular distance (δ) between the two parallel planes defined by the phenyl groups.

TABLE 2

Metal–hydroxyoxime complex bond lengths [a]

Complex	M–O	M–N	C=N	N–O	O··O	Ref.
$Ni(Hbox)_2$	1.83	1.86	1.40 [b]	1.34	2.52	106
$Cu(Hbox)_2$	1.92	1.94	1.25	1.45	2.58	117
$Cu(X\text{–}Hbox)_2$ [c]	1.91	1.96	1.26	1.42	2.63	122
$Pd(Hbox)_2$	1.98	1.94	1.29	1.42	2.62	134, 135
$Pd(X\text{–}Hbox)_2$	–	–	–	–	–	134

[a] Determined by X-ray crystal structural analysis. All values in Ångströms (Å). [b] Later refinement reported as 1.29 Å [105]. [c] X = 5-Cl.



XX

The δ values are in the range 0.05–0.13 Å for all of the complexes reported.

(viii) Mössbauer spectroscopy

Mössbauer spectroscopy thus far has only been used to characterize a few iron–hydroxyoxime complexes, but it has been useful for examining the effects of nucleophilic and electrophilic substituents on the π-acceptor properties of the ligands [57,87]. Although the substituent effects on the Mössbauer spectra are not as pronounced as had been hoped, the results indicate clearly the electronic effects on the metal → ligand back bonding in the complexes.

Mössbauer spectroscopy can indeed be a very useful technique for characterizing iron–hydroxyoxime complexes but it will continue to be of limited use for other metals.

(ix) Graphical analyses

A variety of graphical techniques have been used to characterize the reported hydroxyoxime complexes with transition metals. These techniques include Bjerrum–Calvin pH titration [296–298] for the determination of metal–ligand and proton–ligand stability constants [49,118,149,162,164,188, 231], slope ratio, mole ratio, continuous variation and related methods for stoichiometric analyses [24,33,53,81,178,219,227,257] and a number of other titrimetric methods for various analytical information on the structures of the metal complexes.

The potentiometric titration methods have been extremely useful for examining the effects of intramolecular hydrogen bridging on the formation of the metal–chelate complexes. Burger et al. [55], using the Bjerrum–Calvin

technique in conjunction with spectrophotometric and continuous variation methods, have investigated the stability constants for a variety of divalent transition metals with salicylaldoxime and the 5-chloro and 5-nitro derivatives. Their results show that, for many of the complexes, a situation exists in which the order of the successive stability constants is reversed (i.e., log $K_2 >$ log K_1). This has also been shown to be true for a few metal complexes with 2-hydroxy-alkylphenone oximes [188,299]. Burger et al. conclude that the increased stabilization in the complex is a result of the intramolecular hydrogen bonding between the hydroxyoxime ligands, as previously discussed. However, not all hydroxyoxime complexes with transition metals in which intra-ligand hydrogen bridging would be expected, have log $K_2 >$ log K_1 [49,55,118,149,162,164,188,231,239,241]. As a result, Ashbrook [20] argues that the log $K_2 >$ log K_1 situation is unusual and that for those complexes in which the phenomenon is observed, other stabilization factors must be in effect.

Graphical techniques have proven to be invaluable as a supplemental method to direct spectral characterizations for structural analysis of transition metal–hydroxyoxime complexes. Unfortunately, space does not permit a discussion of all of the graphical methods used to characterize these types of metal complexes and the reader is referred to the original articles for full details.

(x) Thermal analyses

Thermal methods of analysis, including differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetric analysis (TGA), have proved to be useful tools for studying the thermal stability of metal complexes. Most of the thermal characterizations performed on the transition metal–hydroxyoxime complexes listed in Table 1 have involved TGA studies on the precipitated complexes to insure complete dryness, without decomposition, prior to gravimetric analysis. However, a few of the studies have been concerned with the fundamental thermal properties of the complexes [66,84,86,91,95,115,199,276].

Liptay et al. [91] and Lumme [95] investigated the thermal stabilities of various divalent metal–salicylaldoximate complexes and found that the thermal stabilities and the solution stabilities oppose each other. Seshagiri and Rao [199] reported the same results for the metal complexes with 2,4-dihydroxyacetophenone oxime. All three studies conclude that the thermal stabilities of the transition metal–hydroxyoxime complexes are independent of the metal–ligand bond strength and are a function only of the size and structure of the hydroxyoxime ligand.

These results suggest that thermal analysis of the solid transition

metal–hydroxyoxime complexes might yield valuable information on the coordinate bond strengths and solution equilibrium properties.

(xi) Miscellaneous methods

A variety of other analytical techniques have been used to characterize the transition metal–hydroxyoxime complexes listed in Table 1, including molecular weight measurements, elemental analyses, electrical conductance measurements, solubility studies and gravimetric analyses. Most of these characterization methods are used according to well established analytical procedures. As a result, in many of the published reports, only the final results are presented without reference to either the experimental procedures or details. For example, molecular weights are often given with only a brief mention of the technique used, e.g., cryoscopy, ebulliometry or vapor pressure osmometry, while electrical conductance measurements are usually reported simply by indicating that the complex is a non-electrolyte in a particular solvent. It is impractical to attempt a discussion of these techniques in the context of this review and the reader is referred to specific analytical texts and to the original articles referenced in Table 1.

E. REACTIVITY

There have been relatively few studies of the reactivity of transition metal–hydroxyoxime complexes. Many of the complexes that have been isolated are coordinately unsaturated and will form adducts with a large number of basic ligands. The majority of the reactivity studies have centered on ligand addition reactions, especially those employing cyclic nitrogen bases. These reactions are reviewed first followed by a brief discussion of the exchange reactions.

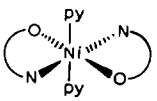
(i) Addition reactions

Addition of pyridine and substituted pyridines to bis-(2-hydroxybenzaldoximato) nickel(II) has been studied extensively by several groups [46,47,60–63]. Willis and Mellor [60] noted that the green diamagnetic nickel–oxime complex becomes paramagnetic when dissolved in pyridine, with a magnetic moment of 3.10 B.M. Since pyridine readily forms adducts with many transition metal complexes, the formation of an octahedral bis-pyridine adduct was proposed (eqn. 15).

$$[Ni(Hbox)_2] + 2\ py \rightarrow [Ni(Hbox)_2(py)_2] \qquad (15)$$

However, all attempts to isolate the pyridine adduct were unsuccessful.

Basolo and Matoush [46], by careful crystallization, succeeded in isolating a yellow-white $[Ni(Hbox)_2(py)_2]$ and characterized the complex by magnetic susceptibility and elemental analysis. They proposed that the complex is octahedral (**XXI**) with the two pyridine molecules occupying *trans* axial positions.

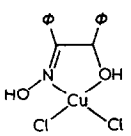


XXI

The structure was confirmed subsequently to be pseudo-octahedral (D_{2h} symmetry) by unambiguous assignments of the electronic absorption spectra [47,62,63].

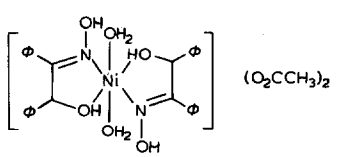
Romano et al. [47,63,64] examined the magnetic and spectrophotometric properties of the adducts of bis-(2-hydroxybenzaldoxime) nickel(II) with a variety of picolines and cyclomethyleneimines and found that, in all cases, pseudo-octahedral bis-base adducts are formed with varying stability constants depending upon the types of strain encountered within the molecule.

Jennings et al. [260] reported the isolation of a green crystalline complex upon treatment of the amorphous polymeric Cu(II)–(α-benzoin oximate) complex with alcoholic HCl. They assigned a tentative structure (**XXII**) to the complex in which the hydroxyoxime is functioning as a neutral bidentate ligand.



XXII

Rindorf [262] confirmed the monomeric nature of the complex by showing that the anomalous magnetic moment of the α-benzoin oximate precursor is normalized upon addition of the two HCl molecules. Jennings et al. [260] also isolated a bis-aquo salt of Ni(II)–(α-benzoin oximate) (**XXIII**) upon



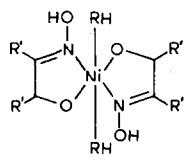
XXIII

acidification of bis-(α-benzoin oximato) nickel(II) with acetic acid in aqueous solution.

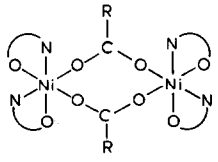
As with the Cu(II)–(α-benzoin oximate)–HCl adduct, the oxime is coordinated as a neutral ligand in which both the hydroxyl and oxime groups are protonated.

A similar bonding situation is found in the Fe(III)–salicylaldoxime system [88]. In strongly acidic media the complex exists only as $[Fe(H_2box)]^{3+}$. However, under basic conditions the complex begins to add hydroxyl groups in a stepwise manner to give a series of complexes of the type $[Fe(Hbox)(OH)_n]^{(3-n)+}$. At sufficiently high pH, the phenolic proton dissociates, resulting in the formation of the $[Fe(Hbox)(OH)_3]^-$ complex anion. The structure and composition of the Co(III), Cu(II) and Ni(II) salicylaldoxime complexes also have been examined under high pH conditions [99] and while the formation of complex anionic species was confirmed, no hydroxyl addition complexes were observed.

The reaction of $[Ni(R,R'-Hox)_2]$ (R,R' = n-BuCH(Et)) with lauric acid (RH) in hexane has been examined by Flett et al. [37] using spectrophotometric titration. They report the formation of the six-coordinate $[Ni(R,R'-Hox)_2(RH)_2]$ bis-acid adduct complex. Although no structure was proposed, the reported electronic absorption spectrum indicates that it has octahedral or pseudo-octahedral geometry (**XXIV**).



XXIV



XXV

The solubility of the complex in hexane precludes assignment of a complex salt structure similar to (**XXIII**). However, a structure with bridging carboxylate ligands (**XXV**) cannot be ruled out based on the spectral results presented.

(ii) Exchange reactions

The exchange of Ni(II) and Co(II) between the salicylaldoxime complexes and the metal ions in solution have been investigated using radio-isotopes [98,103,300]. West [98] has shown that the bis-(salicylaldoximato) cobalt(II) complex, in pyridine solution, undergoes complete exchange within 18 min when deoxygenated and less than 15% exchange after 60 min in oxygenated solution. The difference in rates was attributed to the formation of an

oxygen adduct complex in solution but no mechanistic information was given. Hall et al. [103,300] have found even faster metal exchange rates in the bis-(salicylaldoximato) nickel(II) complex with complete exchange in less than five min in 2-methoxy-ethanol. The results of these studies have been interpreted in terms of the metal–ligand bonding with slow exchange explained in terms of partial ionic character.

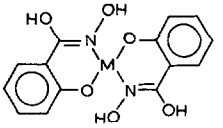
F. OTHER COMPLEXES

Because of the requirements we set at the beginning concerning the scope of this review, we had to exclude several interesting classes of hydroxyoximes. The two most noticeable omissions are the salicylhydroxamic acids and the salicylamidoximes. Since complexes with these ligands may be of interest to some readers, a few are briefly mentioned here, although this section is not meant to be comprehensive.

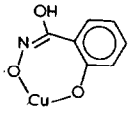
(i) Salicylhydroxamic acids

As with salicylaldoxime, salicylhydroxamic acid complexes with transition metals were first prepared as a result of the use of the oxime as a gravimetric reagent for the detection and determination of various metals in aqueous solution [301–303]. Although these reports were not concerned primarily with structural analyses, a few structures were proposed based on analogy to known salicylaldoxime complexes.

Bhaduri [302] investigated the reaction of salicylhydroxamic acid with thirteen transition metals and proposed a four-coordinate structure (**XXVI**) for many of the divalent metal complexes.



XXVI

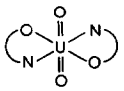


XXVII

However, the copper(II) and cadmium(II) complexes were assigned structure (**XXVII**), involving an unlikely seven-member ring in which the hydroxamic

acid is functioning as a dibasic ligand.

Using electronic absorption and graphical techniques, Bhaduri and Ray [303] proposed that the orange-yellow uranium(VI)–salicylhydroxamic acid complex has structure (**XXVIII**), identical to the salicylaldoxime complex.



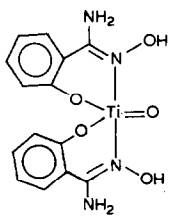
XXVIII

Molybdenum(VI), vanadium(V) and iron(III) complexes were also examined but no structures were suggested.

Chakraburtty et al. [304–306] examined the complex formation between salicylhydroxamic acid and a variety of metals including iron(III), nickel(II), cobalt(II), manganese(II), uranium(VI), molybdenum(VI), titanium(IV), niobium(V), tantalum(V) and zirconium(IV). Using a variety of graphical techniques, stoichiometries were proposed for many of the complexes but no structural assignments were made.

(ii)Salicylamidoximes

The reactions of salicylamidoxime with transition metals have been limited mainly to its application as an analytical reagent [307–311], and most of the studies have dealt with gravimetric analyses. Bandyopadhayay et al. [307–310] have examined the stoichiometry of the copper(II), nickel(II), iron(III) and uranium(VI) complexes with salicylaldoxime using graphical techniques but no structures were proposed. However, the titanium(IV) complex [311] has been proposed as five coordinate (**XXIX**) based on elemental analysis and analogy to the known salicylaldoxime complexes.



XXIX

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REFERENCES

1 L. Tschugaeff, Chem. Ber., 38 (1905) 2520.
2 F. Feigl, Chem. Ber., 56 (1923) 2083.
3 F. Ephraim, Chem. Ber., 63 (1930) 1928.
4 F.J. Welcher, Organic Analytical Reagents, Van Nostrand, New York, NY, 1947.
5 K. Burger, Organic Reagents in Metal Analysis, Pergamon, Oxford, 1973.
6 F. Feigl, Chemistry of Specific, Selective and Sensitive Reactions, Academic Press, New York, NY, 1947.
7 A.E. Martell and M. Calvin, Chemistry of the Metal Chelate Compounds, Prentice-Hall, Englewood Cliffs, NJ, 1952.
8 J.C. Bailar and D.H. Busch, The Chemistry of the Coordination Compounds, Reinhold, New York, NY, 1956.
9 B. Egneus, Talanta, 19 (1972) 1387.
10 A. Chakavorty, Coord. Chem. Rev., 13 (1974) 1.
11 R.B. Singh, B.S. Garg and R.P. Singh, Talanta, 26 (1979) 425.
12 R.C. Mehrota, A.K. Rai, A. Singh and R. Bohra, Inorg. Chim. Acta, 13 (1975) 91.
13 A. Singh, V.D. Gupta, G. Srivastava and R.C. Mehrota, J. Organomet. Chem., 64 (1974) 145.
14 A.K. Babko, Nauk. Zap. Kievsk, Univ. Im. T.G. Schevchenka, (1956) 241.
15 C.V. Banks, Proc. Int. Symp. Anal. Chem., 1 (1963) 131.
16 C.V. Banks, Rec. Chem. Prog., 25 (1964) 85.
17 D. Dryssen, Sven. Kem. Tidskr., 75 (1963) 618.
18 V.M. Peshkova, V.M. Sasvostina and E.K. Ivanova, Analytical Reagents: Oximes, Nauka, Moscow, 1977.
19 A.J. Van der Zeeuw and R. Kok, CIM Spec., Vol. 21 (1979) (1, Proc. Int. Solvent Extr. Conf., 1977), p. 17.
20 A.W. Ashbrook, Coord. Chem. Rev., 16 (1975) 285.
21 A.W. Ashbrook, Hydrometallurgy, 1 (1975) 5.
22 R.R. Swanson, CIM Spec. Vol. 21 (1979) (1, Proc. Int. Solvent Extr. Conf., 1977), p. 3.
23 J.M. Pratt and R.I. Tilley, Hydrometallurgy, 5 (1979) 29.
24 J.S. Preston, J. Inorg. Nucl. Chem., 37 (1975) 1235.
25 J.S. Preston, J. Inorg. Nucl. Chem., 42 (1980) 441.
26 I. Dahl, Anal. Chim. Acta, 41 (1968) 9.
27 R.J. Whewell and C. Hanson, Ion Exch. Solvent Extr., 8 (1981) 1.
28 D.R. Nagaraj and P. Somasundaran, Trans. Soc. Min. Eng. AIME, 266 (1977) 1892.
29 D.R. Nagaraj and P. Somasundaran, Min. Eng. (Littleton, CO), 33 (1981) 1351.
30 D.R. Nagaraj and P. Somasundaran, Recent Dev. Sep. Sci., 5 (1979) 81.
31 C.C. DeWitt and F. von Batchelder, J. Am. Chem. Soc., 61 (1939) 1247; 61 (1939) 1250.
32 J.A. Milner and R.M. Turner, Brit. U.K. Pat. Appl. 2, 009, 626 (Imperial Chemical Ind. Ltd.) 20 June, 1979.
33 K. Osseo-Asare and D.R. Renninger, Hydrometallurgy, in press.
34 S.O. Fekete, G.A. Meyer and G.R. Wicker, The Metallurgical Society AIME Preprint No. A77-95 (1977); U.S. Pat. 4193969, 18 March, 1980.

35 K. Osseo-Asare, H.L. Leaver and J.M. Laferty, in M.C. Kuhn (Ed.), Process and Fundamental Considerations of Selected Hydrometallurgical Systems, SME-AIME, New York, NY, 1981, pp. 195–207.
36 L.V. Gallacher, U.S. Pat. 4018865, 19 April, 1977.
37 D.S. Flett, M. Cox and J.D. Heels, Proc. Int. Solvent Extr. Conf., (1974), Soc. Chem. Ind., London, 1974, Vol. 3, p. 2559.
38 D.S. Flett and D.W. West, Proc. Int. Solvent Extr. Conf., (1971), Soc. Chem. Ind., London, 1971, Vol. 1, p. 214.
39 T. Tammi, Tutkimus Tek., (1976) 44; Chem. Abstr., 89 (1978) 11 8498.
40 D.S. Flett and S. Titmuss, J. Inorg. Nucl. Chem., 31 (1969) 2612.
41 M. Cox and D.S. Flett, Proc. Int. Solvent Extr. Conf., (1971), Soc. Chem. Ind., London, 1971, Vol. 1, p. 204.
42 K. Osseo-Asare and M.E. Keeney, Metall. Trans. B, 11 (1980) 63.
43 K. Osseo-Asare and M.E. Keeney, Sep. Sci. Technol., 15 (1980) 999.
44 K. Osseo-Asare and M.E. Keeney, Proc. Int. Solvent Extr. Conf., (1980), Assoc. Ing. Sortis Univ. Liège, Liège, Belgium, 1980, Vol. 1, paper 80-121.
45 K. Osseo-Asare, D.R. Renninger and J.D. Wagner, Solvent Extr. Ion Exch., 1 (1983) 337.
46 F. Basolo and W.R. Matoush, J. Am. Chem. Soc., 75 (1953) 5663.
47 V. Romano, F. Maggio and T. Pizzino, J. Inorg. Nucl. Chem., 33 (1971) 2611.
48 N.S. Biradar and V.B. Mahale, J. Less-Common Met., 31 (1973) 159.
49 S. Mahdal and A.K. Dey, J. Inorg. Nucl. Chem., 30 (1968) 1221; 31 (1969) 896.
50 H.J. Bielig and E. Bayer, Liebig's Ann. Chem., 580 (1953) 135; 584 (1953) 96.
51 N.S. Biradar and S.D. Angadi, Rev. Roum. Chim., 20 (1975) 755.
52 H.J. Bielig and H. Mollinger, Liebig's Ann. Chem., 605 (1957) 117.
53 M.S. Kachhawala and A.K. Bhattacharya, Z. Anorg. Allg. Chem., 325 (1963) 321.
54 K. Burger and I. Egyed, J. Inorg. Nucl. Chem., 27 (1965) 2361.
55 K. Burger, F. Ruff, I. Ruff and I. Egyed, Acta Chim., 46 (1965) 1.
56 K.K. Ramaswamy, C.I. Jose and D.N. Sen, Indian J. Chem., 5 (1967) 156.
57 J.L.K.F. de Vries, J.M. Trooster and E. de Boer, Chem. Commun., (1970) 604.
58 C.A. Fleming, B.R. Green and K.G. Ashurst, Proc. Int. Solvent Extr. Conf., (1980), Assoc. Ing. Sortis Univ. Liège, Liège, Belgium, 1980, Vol. 2, paper 80-224.
59 I. Rami, K.B. Pandeya, G.L. Sawhney and J.S. Bailjal, Acta Chim. Acad. Sci. Hung., 110 (1982) 75.
60 J.B. Willis and D.P. Mellor, J. Am. Chem. Soc., 69 (1947) 1237.
61 H.C. Clark and A.L. Odell, Chem. Ind., (1954) 1510.
62 J. Csaszar, Acta Chim., 32 (1962) 343.
63 F. Maggio, V. Romano, T. Pizzino and L. Pellerito, Ann. Chim., 58 (1968) 725.
64 V. Romano, T. Pizzino, L. Pellerito and F. Maggio, Ann. Chim., 59 (1969) 828.
65 J.W. Hosking and N.M. Rice, Hydrometallurgy, 3 (1978) 217.
66 P. Lumme and P. Knuuttila, J. Therm. Anal., 25 (1982) 139.
67 U.K. Jetley, J. Singh and S.M. Rastogi, Bangladesh J. Sci. Ind. Res., 16 (1981) 134; Chem. Abstr., 98 (1983) 118694f.
68 G.A. Yagodin, V.V. Sergievskii, V.I. Kuz'min and G.L. Parshkov, Russ. J. Inorg. Chem., 26 (1981) 108; Zh. Neorg. Khim., 26 (1981) 205.
69 B.M. Laskorin, V.V. Yaksin, V.S. Ul'yanov and A.M. Minokhin, Proc. Int. Solvent Extr. Conf., (1974), Soc. Chem. Ind., London, 1974, Vol. 2, p. 1775.
70 A.F. Morgunov, G.I. Nasonova, A.G. Budanov and Yu G. Frolov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 23 (1980) 807.
71 M.E. Keeney and K. Osseo-Asare, Proc. Int. Solvent Extr. Conf., (1983), AIChE, New York, 1983, p. 345.

72 L. Hummelstedt, E. Paatero, T. Nyberg and L. Rosenback, Proc. Int. Solvent Extr. Conf., (1980), Assoc. Ing. Sortis Univ. Liège, Liège, Belgium, 1980, Vol. 2, paper 80-73.
73 D.S. Flett, D.N. Okuhara and D.R. Spink, J. Inorg. Nucl. Chem., 35 (1973) 2471.
74 V.I. Lakshmanan and G.J. Lawson, J. Inorg. Nucl. Chem., 37 (1975) 207.
75 R.L. Atwood and J.D. Miller, Trans. Soc. Min. Eng. AIME, 254 (1973) 319.
76 C. Nie and P. Yao, Huaxue Xuebao, 39 (1981) 727; Chem. Abstr., 98 (1983) 9601c.
77 B.K. Deshmukh, J. Indian Chem. Soc., 60 (1983) 203.
78 M. Kamini, F. Kamil and S.K. Sindhwani, J. Chin. Chem. Soc. (Taipei), 29 (1982) 209.
79 M. Kamini, S.K. Sindhwani and R.P. Singh, Analusis, 10 (1982) 390.
80 M. Kamini, S.K. Sindhwani and R.P. Singh, Ann. Chim., 73 (1983) 223.
81 D.R. Renninger and K. Osseo-Asare, Metall Trans. B, 14 (1983) 41.
82 M.E. Keeney and K. Osseo-Asare, Proc. Int. Solvent Extr. Conf., (1980), Assoc. Ing. Sortis Univ. Liège, Liège, Belgium, 1980, Vol. 1, paper 80-53.
83 M.E. Keeney and K. Osseo-Asare, Polyhedron, in press.
84 M.E. Keeney and K. Osseo-Asare, Polyhedron, submitted.
85 T.T. Tammi, Hydrometallurgy, 2 (1976/1977) 371.
86 P. Lumme and M.L. Korvola, Thermochim. Acta, 13 (1975) 419.
87 K. Burger, L. Korecz, I.B.A. Manuaba and P. Mag, J. Inorg. Nucl. Chem., 28 (1966) 1673.
88 K.R. Manolov, Russ. J. Inorg. Chem., 12 (1967) 1431.
89 A.K. Ray and P. Ray, Proc. Symp. Coord. Compounds, 3 (1960) 200.
90 M.N. Desai, K.C. Desai and M.H. Ghandi, Indian J. Appl. Chem., 35 (1972) 144.
91 G. Liptay, E. Papp-Molnar and K. Burger, J. Inorg. Nucl. Chem., 31 (1969) 247.
92 O.L. Brady, J. Chem. Soc., (1931) 105.
93 B.N. Figgis and R.S. Nyholm, J. Chem. Soc., (1954) 12.
94 D.P. Mellor and D.P. Craig, J. Proc. R. Soc. N.S.W., 73 (1939) 233.
95 P.O. Lumme, Suom. Kemistil. B, 31 (1958) 253; 32 (1959) 203, 261.
96 H. Nishikawa and S. Yamada, Bull. Chem. Soc. Jpn., 37 (1964) 8.
97 K. Sone, J. Am. Chem. Soc., 75 (1953) 5207.
98 B. West, J. Chem. Soc., (1952) 3115.
99 M. Bobtelsky and E. Jungreis, J. Inorg. Nucl. Chem., 3 (1956) 38.
100 K. Nakamoto, M. Margoshes and R.E. Rundel, J. Am. Chem. Soc., 77 (1955) 6480.
101 E.G. Cox, F.W. Pinkard, W. Wardlaw and K.C. Webster, J. Am. Chem. Soc., (1935) 459.
102 A.K. De and C. Sahu, Sep. Sci., 2 (1967) 11.
103 N.F. Hall and B.R. Willeford, J. Am. Chem. Soc., 73 (1951) 5419.
104 L. Malatesta, Gazz. Chim. Ital., 68 (1938) 319.
105 L.L. Merritt, C. Guare and A.E. Lessor, Acta Crystallogr., 9 (1956) 253.
106 R.C. Srivastava, E.C. Lingafelter and P.C. Jain, Acta Crystallogr., 22 (1967) 922.
107 J.E. Mills and D.P. Mellor, J. Am. Chem. Soc., 64 (1942) 181.
108 Y. Yamamoto, K. Ueda and S. Ueda, J. Chem. Soc. Jpn., Pure Chem. Sect., 89 (1968) 288.
109 R. Milosevic and J. Hojman, Acta Pharm., 29 (1979) 35.
110 D.P. Goel, K.C. Trikha and R.P. Singh, Proc. Indian Acad. Sci., Sect. A, 68 (1968) 82.
111 A.K. Ray and P. Ray, J. Indian Chem. Soc., 37 (1960) 133.
112 A.K. Mukherjee, Anal. Chim. Acta, 13 (1955) 334.
113 F. Buscarons and M. Blanco, Quim. Anal., 29 (1975) 99.
114 P.N.M. Das and C.P. Trivedi, Indian J. Chem., 11 (1973) 699.
115 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.
116 R. Hara and P.W. West, Anal. Chim. Acta, 15 (1956) 193.

117 M.A. Jarski and E.C. Lingafelter, Acta Crystallogr., 17 (1964) 1109.
118 K.E. Jabalpurwala, K.A. Venkatachalam and M.B. Kabadi, J. Inorg. Nucl. Chem., 26 (1964) 1027.
119 P. Ray and D.N. Sen, J. Indian Chem. Soc., 25 (1948) 473.
120 S.H. Simonsen and H.M. Burnett, Anal. Chem., 27 (1955) 1336.
121 G. Schoffa, O. Ristau and B.E. Wahler, Z. Phys. Chem., 215 (1960) 203.
122 P.L. Orioli, E.C. Lingafelter and B.W. Brown, Acta Crystallogr., 17 (1964) 1113.
123 D. Stpeniak-Biniakiewicz and J. Szymanowski, J. Chem. Technol. Biotechnol., 29 (1979) 686.
124 S.H. Simonsen and P. Christopher, Anal. Chem., 26 (1954) 682.
125 J. Rynasiewicz and J.F. Flagg, Anal. Chem., 26 (1954) 1506.
126 J.F. Flagg and N.H. Furman, Ind. Eng. Chem., Anal. Ed., 12 (1940) 663.
127 T.G. Pearson, Fresenius Z. Anal. Chem., 112 (1938) 179.
128 L.P. Biefeld and W.B. Ligett, Ind. Eng. Chem., Anal. Ed., 14 (1942) 359.
129 Z. Holzbecher, Collect. Czech. Chem. Commun., 24 (1959) 3915.
130 R.R. Naidu, Curr. Sci., 36 (1967) 150.
131 R. Ripan, Z. Szekely and G. Kiss-Imreh, Rev. Roum. Chim., 13 (1968) 1313.
132 M. Blanco, Ion (Madrid), 35 (1975) 507.
133 M. Gahide, Bull. Soc. Chem. Belg., 45 (1936) 9.
134 C.E. Pfluger, Ph.D. Thesis, University of Texas, 1958.
135 C.E. Pfluger and R.L. Harlow, Acta Crystallogr., Sect. B, 26 (1970) 1631.
136 M.J. Cleare, P. Charlesworth and D.J. Bryson, J. Chem. Technol. Biotechnol., 29 (1979) 210.
137 D.P. Goel, K.C. Trikha and R.P. Singh, Curr. Sci., 39 (1967) 517.
138 D.P. Goel, K.C. Trikha and R.P. Singh, Indian J. Appl. Chem., 32 (1969) 62.
139 N.S. Biradar, M.D. Patil and T.R. Goudar, J. Inorg. Nucl. Chem., 37 (1975) 1435.
140 A.K. Ray and P. Ray, J. Indian Chem. Soc., 37 (1960) 141.
141 S.N. Poddar, Indian J. Appl. Chem., 26 (1963) 153.
142 L.C. Jhaveri, G.S. Patel and V.M. Thakor, J. Gujarat Univ., 18 (1975) 70.
143 N.S. Biradar, M.D. Patil and V.B. Mahale, Curr. Sci., 44 (1975) 414.
144 S. Prakash, Y. Dutt and R.P. Singh, Indian J. Chem., 7 (1969) 512.
145 N. Singh, B.D. Kansal, A.C. Ojha and H. Singh, J. Indian Chem. Soc., 56 (1979) 840.
146 L.C. Jhaveri, G.S. Patel and V.M. Thakor, J. Indian Chem. Soc., 53 (1976) 1147.
147 S. Praskash, Y. Dutt and R.P. Singh, Indian J. Chem., 8 (1970) 460.
148 N.S. Biradar, S.D. Angadi and V.B. Mahale, Curr. Sci., 44 (1975) 539.
149 D.B. Ingle and D.D. Khanolkar, J. Indian Chem. Soc., 50 (1973) 25.
150 R.N. Saksena and K.K. Panday, J. Indian Chem. Soc., 50 (1973) 609.
151 S.N. Poddar, Fresenius Z. Anal. Chem., 154 (1957) 254.
152 S.N. Poddar, Indian J. Chem., 1 (1963) 537.
153 S.N. Poddar, J. Indian Chem. Soc., 40 (1963) 706.
154 K.L.C. Jhaveri and H.B. Naik, J. Inst. Chem., 49 (1977) 80.
155 N. Singh, B.D. Kansal, A.C. Ojha, H. Singh and H.D. Tayal, J. Indian Chem. Soc., 56 (1979) 189.
156 K. Lal and S.P. Gupta, Chem. Era, 12 (1976) 414.
157 K.L.C. Jhaveri and H.B. Naik, J. Indian Chem. Soc., 56 (1979) 639.
158 S. Prakash, Y. Dutt and R.P. Singh, J. Inst. Chem., 41 (1969) 182.
159 S. Prakash, Y. Dutt and R.P. Singh, Indian J. Appl. Chem., 32 (1969) 59.
160 M. Katyal, S. Prakash and R.P. Singh, Indian J. Chem., 4 (1966) 94.
161 J. Singh and S.P. Gupta, Acta Cienc. Indica, 1 (1974) 107.

162 D.B. Ingle and D.D. Khanolkar, Indian J. Chem., Sect. A, 14 (1976) 596.
163 B.H. Patel, J.R. Shah and R.P. Patel, J. Indian Chem. Soc., 52 (1975) 998.
164 V.S. Babu, D.U. Raju and R.R. Naidu, Indian J. Chem., Sect. A, 18 (1979) 87.
165 S.N. Poddar, Indian J. Chem., 1 (1963) 496.
166 K.S. Bhatki, A.T. Rane and M.B. Kabadi, Proc. Symp. Chem. Coord. Compounds, 3 (1960) 78.
167 G.R. Reddy, S.G. Kadarmandalgi and A.S.R. Murthy, Proc. Indian Acad. Sci., Sect. A, 59 (1964) 159.
168 G.S. Chowdar and N. Appalaraju, Curr. Sci., 44 (1975) 343.
169 K. Lal, J. Singh and S.P. Gupta, Rec. Port. Quim., 20 (1978) 10.
170 L.D. Dave and U.K. Malla, Vidya, 15 (1972) 129.
171 M.N. Desai and M.H. Gandhi, Chem. Ind., 20 (1968) 653.
172 M.H. Gandhi and M.N. Desai, J. Indian Chem. Soc., 45 (1968) 484.
173 J. Singh and S.P. Gupta, Curr. Sci., 44 (1975) 612.
174 M.H. Gandhi and M.N. Desai, Anal. Chem., 39 (1967) 1643.
175 S. Prakash, Y. Dutt and R.P. Singh, Microchem. J., 18 (1973) 412.
176 M.H. Gandhi and M.N. Desai, Chim. Anal., 50 (1968) 167.
177 M.H. Gandhi and M.N. Desai, Indian J. Appl. Chem., 32 (1969) 360.
178 J. Singh, S.P. Gupta and O.P. Malik, Indian J. Chem., 13 (1975) 1217.
179 P.V. Takalkar and V.R. Rao, J. Inorg. Nucl. Chem., 37 (1975) 2103.
180 V.D. Khanolkar and D.D. Khanolkar, Indian J. Chem., Sect. A, 18 (1979) 359.
181 V. Seshagiri and S.B. Rao, Aust. J. Chem., 20 (1967) 2783.
182 H. Singh and K.C. Sharma, Indian J. Appl. Chem., 28 (1965) 43.
183 K. Lal and S.P. Gupta, Indian J. Chem., 13 (1975) 973.
184 S.P. Gupta, S.K. Srivastava and K. Lal, Indian J. Chem., 13 (1975) 297.
185 K. Lal and S.P. Gupta, Curr. Sci., 44 (1975) 178.
186 S. Prakash, H. Singh and M.P. Gupta, J. Proc. Inst. Chem., 38 (1966) 125.
187 S. Prakash, Y. Dutt and R.P. Singh, Indian J. Chem., 6 (1968) 664.
188 B.H. Patel, J.R. Shah and R.P. Patel, J. Indian Chem. Soc., 52 (1975) 998.
189 J. Singh and S.P. Gupta, Acta Cienc. Indica, 3 (1977) 112.
190 S. Kiciak, S. Magas, T. Malinski, A. Lewandowski, M. Kostanski, J. Malinska and Z. Swit, Zesz. Nauk. Politech. Slask., Chem., 88 (1979) 163.
191 T.S. Reddy and S.B. Rao, Talanta, 26 (1979) 968.
192 S.N. Poddar, Fresenius' Z. Anal. Chem., 155 (1957) 327.
193 V.D. Khanolkar and D.D. Khanolkar, Indian J. Chem., Sect. A, 18 (1979) 315.
194 V.V. Balakrishna, R.C. Hussain and N.A. Raju, Proc. Indian Acad. Sci., Sect. A, 87 (1978) 291.
195 K.S. Bhatki, A.T. Rane and M.B. Kabadi, Proc. Indian Acad. Sci., Sect. A, 58 (1963) 202.
196 K.S. Bhatki, A.T. Rane and M.B. Kabadi, Bull. Chem. Soc. Jpn., 36 (1963) 1689.
197 Y.K. Reddy, Curr. Sci., 35 (1966) 64.
198 Y.K. Reddy, Proc. Indian Acad. Sci., Sect. A, 61 (1965) 368.
199 V. Seshagiri and S.B. Rao, Fresenius Z. Anal. Chem., 262 (1972) 275.
200 K.L.C. Jhaveri, G.S. Patel and V.M. Thakor, J. Indian Chem. Soc., 52 (1975) 730.
201 S.M. Patel and H.B. Naik, J. Indian Chem. Soc., 52 (1975) 997.
202 B.D. Gupta and W.U. Malik, Indian J. Appl. Chem., 32 (1969) 348.
203 L.D. Dave and J. D'sa, Vidya, 15 (1972) 132.
204 L.D. Dave and U.K. Malla, Vidya, 15 (1972) 129.
205 P.C. Trivedi and B.C. Haldar, J. Indian Chem. Soc., 50 (1973) 81.
206 S.P. Gupta and K. Lal, Acta Cienc. Indica, 2 (1976) 119.

207 R.N. Saksena and K.K. Panday, Indian J. Appl. Chem., 35 (1972) 61.
208 J.S. Dave and A.R. Patel, J. Sci. Ind. Res., Sect. B, 20 (1961) 81.
209 K.C. Trikha, S. Prakash and R.P. Singh, Curr. Sci., 35 (1966) 175.
210 J.S. Dave and A.R. Patel, Curr. Sci., 31 (1962) 148.
211 S.P. Gupta, O.P. Malik and J. Singh, J. Indian Chem. Soc., 52 (1975) 956.
212 S.N. Poddar and K. Ray, J. Indian Chem. Soc., 46 (1969) 216.
213 K.S. Bhatki, A.T. Rane and M.B. Kabadi, Proc. Symp. Chem. Coord. Compounds, 3 (1960) 87.
214 A. Kapahi, K.B. Pandeya and R.P. Singh, Indian J. Chem., Sect. A, 14 (1976) 444.
215 K.A. Reddy and Y.K. Reddy, Proc. Indian Acad. Sci., 74 (1971) 153.
216 J.S. Dave and A.R. Patel, Curr. Sci., 29 (1960) 472.
217 K.L.C. Jhaveri, G.S. Patel and V.M. Thakor, Chem. Era, 11 (1976) 29.
218 K.L.C. Jhaveri, H.B. Naik, G.S. Patel and V.M. Thakor, Chem. Era, 12 (1976) 287.
219 B.D. Gupta and W.U. Mallik, Indian J. Chem., 7 (1969) 724.
220 K. Lal and S.P. Gupta, Curr. Sci., 45 (1976) 84.
221 S.N. Poddar, Anal. Chim. Acta, 28 (1963) 586.
222 V.V. Balakrishna and N.A. Raju, Curr. Sci., 48 (1979) 724.
223 K.S. Bhatki and A.T. Rane, Solvent Extr. Chem., Proc. Int. Conf., Gothenburg, 1966, D. Dyrssen, J.-O. Litjenzin and J. Rydberg, (Eds.), North-Holland, Amsterdam, 1967, p. 147.
224 G.R. Reddy, Curr. Sci., 36 (1967) 665.
225 K.L.C. Jhaveri and H.B. Naik, J. Indian Chem. Soc., 55 (1978) 183.
226 U.K. Jetley, J. Singh and S.N. Rastogi, Chem. Era, 15 (1979) 23.
227 K. Lal and S.P. Gupta, Curr. Sci., 44 (1975) 652.
228 K.L.C. Jhaveri and H.B. Naik, J. Inst. Chem., 51 (1979) 219.
229 S. Prakash, R.P. Singh and K.C. Trikah, Talanta, 13 (1966) 1393.
230 J. Singh and S.P. Gupta, Indian J. Chem., Sect. A, 14 (1976) 710.
231 D.B. Ingle and D.D. Khanolkar, J. Indian Chem. Soc., 50 (1973) 103.
232 S.N. Poddar, Indian J. Appl. Chem., 27 (1964) 67.
233 S. Kiciak, Chem. Anal., 23 (1978) 382, 615.
234 S. Przeszlakowski, Chem. Anal., 22 (1977) 877.
235 K.S. Koppiker and A.B. Chakraborty, Indian J. Technol., 13 (1975) 529.
236 N.S. Bhave and R.B. Kharat, J. Indian Chem. Soc., 56 (1979) 244.
237 B.K. Deshmukh, C.N. Vyas and R.B. Kharat, J. Indian Chem. Soc., 52 (1975) 385.
238 B.K. Deshmukh, S.B. Gholse and R.B. Kharat, Fresenius Z. Anal. Chem., 279 (1976) 363.
239 B.K. Deshmukh and R.B. Kharat, J. Inorg. Nucl. Chem., 39 (1977) 165.
240 B.K. Deshmukh and R.B. Kharat, Indian J. Chem., Sect. A, 14 (1976) 214.
241 B.K. Deshmukh and R.B. Kharat, J. Indian Chem. Soc., 53 (1976) 1067; 56 (1979) 213.
242 R.S. Naidu and R.R. Naidu, Talanta, 25 (1978) 354.
243 S.I. Gusev, V.I. Kumov and E.V. Sokolova, Zh. Anal. Khim., 15 (1960) 180.
244 M. Michio, J. Chem. Soc. Jpn., Pure Chem. Sect., 80 (1959) 1270.
245 R.S. Naidu and R.R. Naidu, Indian J. Chem., Sect. A, 15 (1977) 69.
246 K. Uesugi and S. Yamaguchi, Bunseki Kagaku, 28 (1979) 268.
247 R.C. Hussain and N.A. Raju, Proc. Indian Acad. Sci., Sect. A, 84 (1976) 144.
248 D.N. Patkar and R.N. Merchant, J. Indian Chem. Soc., 56 (1979) 194.
249 V.V. Balakrishna and N.A. Raju, Curr. Sci., 49 (1980) 227.
250 N.D. Tambat and R.N. Merchant, J. Indian Chem. Soc., 45 (1968) 517.
251 D.N. Patkar, N.D. Tambat and R.N. Merchant, Curr. Sci., 42 (1973) 818.

252 H.G. Lakhani, G.R. Dave and M.N. Vakharia, J. Inst. Chem., 41 (1969) 122.
253 T. Momose and Y. Ohkura, Bunseki Kagaku, 5 (1956) 332.
254 A.D. Nejkar, S.B. Padhye and B.A. Kulkarni, J. Univ. Poona, Sci. Technol., 48 (1976) 277.
255 S. Goszczynski, J. Szymanowski, A. Borowiak and J. Blaszczak, Indian J. Technol., 17 (1979) 77.
256 J.F. Flag and N.H. Furman, Ind. Eng. Chem., Anal. Ed., 12 (1940) 529.
257 H.J. Hoenes and K.G. Stone, Talanta, 4 (1960) 250.
258 L. Malatesta, Gazz. Chim. Ital., 68 (1938) 319.
259 R. Pastorek and V. Bortlova, Acta Univ. Palacki Olomuc., Fac. Rerum Nat., 57 (1978) 29.
260 J.S. Jennings, E. Sharratt and W. Wardlaw, J. Chem. Soc., (1935) 818.
261 J. Mironoff, Bull. Soc. Chem. Belg., 45 (1936) 1.
262 G. Rindorf, Acta Chem. Scand., 25 (1971) 774.
263 J.S. Fritz and D.R. Beuerman, Anal. Chem., 44 (1972) 692.
264 J.S. Fritz, D.R. Beuerman and J.J. Richard, Talanta, 18 (1971) 1095.
265 H.A. Sutter and P.W. West, Anal. Chim. Acta, 13 (1955) 501.
266 F. Feigl, G. Sicher and O. Singer, Chem. Ber., 58 (1925) 2294.
267 J.V. Dubsky and A. Langer, Chem. Obz., 13 (1939) 178.
268 A. Langer, Ind. Eng. Chem., Anal. Ed., 14 (1942) 283.
269 H.B. Knowles, Bur. Standards J. Res., 9 (1932) 1.
270 S. Ishibash, J. Chem. Soc. Jpn., 61 (1932) 125.
271 P.K. Paria and S.K. Majumdar, Fresenius Z. Anal. Chem., 279 (1976) 207.
272 V.R. Rao and P.R. Murty, Indian J. Chem., 6 (1968) 465.
273 B. Soptrajanov, A. Nikolovski and I. Petrov, Spectrosc. Lett., 1 (1968) 117.
274 B.D. Gupta and W. Malik, J. Indian Chem. Soc., 48 (1971) 59.
275 R. Bohra, A.K. Rai and R.C. Mehrota, Indian J. Chem., 12 (1974) 855.
276 R. Pastorek, Monatsh. Chem., 103 (1972) 831.
277 H.B. Naik, L.C. Jhaveri, G.S. Patel and V.M. Thakor, J. Inst. Chem., 50 (1978) 168, 156.
278 N.S. Biradar, V.B. Mahale and V.H. Kulkarni, J. Inorg. Nucl. Chem., 35 (1973) 2565.
279 L.C. Jhaveri, H.B. Naik, G.S. Patel and V.M. Thakor, Chem. Era, 14 (1978) 39.
280 R. Pastorek and V. Bortlova, Acta Univ. Palacki Olomuc., Fac. Rerum Nat., 53 (1977) 19.
281 K. Goswami and M.M. Singh, J. Inorg. Nucl. Chem., 39 (1977) 1718.
282 R.F. Pietrzak and L. Gordon, Talanta, 9 (1962) 327.
283 B.S.K. Rao and O.E. Hileman, Talanta, 14 (1967) 299.
284 E.L. Bickerdike and H.H. Willard, Anal. Chem., 24 (1952) 1026.
285 L. Gordon, M.L. Salutsky and H.H. Willard, Precipitation from Homogeneous Solution, Wiley, New York, NY, 1959.
286 F.H. Firsching, Adv. Anal. Chem. Instrum., 4 (1965) 1.
287 K. Fujimori, H. Okino and T. Ogata, Jpn. Kokai Tokkyo Koho 79, 112, 303, Sep. 1979.
288 H. Irving and R.J.P. Williams, Treatise on Analytical Chemistry, Part 1, Vol. 3, I.M. Kolthoff and P.J. Elving (Eds.), Interscience, New York, 1961, p. 1309.
289 T. Sekine and Y. Hasegawa, Solvent Extraction Chemistry, M. Dekker, New York, NY, 1977.
290 D.S. Flett, Acc. Chem. Res., 10 (1977) 99.
291 D.S. Flett, Soc. Min. Eng. Preprint No. 79-34, (1979).
292 J. Charalambous, Mass Spectrometry of Metal Compounds, Butterworths, Boston, MA, 1975.

293 R.E. Rundle and M. Parasol, J. Chem. Phys., 20 (1952) 1487.
294 L. Sacconi, Transition Met. Chem., 4 (1968) 199.
295 K. Nakamoto and P.J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, Wiley, New York, NY, 1968.
296 M. Calvin and N.C. Melchior, J. Am. Chem. Soc., 70 (1948) 3270.
297 M. Calvin and K.W. Wilson, J. Am. Chem. Soc., 67 (1945) 2003.
298 J. Bjerrum, Metal Ammine Formation in Aqueous Solution, Haase, Copenhagen, 1957.
299 L.G. Sillen and A.E. Martell, Stability Constants of Metal-Ion Complexes, The Chemical Society, London, 1964.
300 J.E. Johnson and N.F. Hall, J. Am. Chem. Soc., 70 (1948) 2344.
301 C. Musante, Gazz. Chim. Ital., 78 (1948) 536.
302 A.S. Bhaduri, Fresenius Z. Anal. Chem., 151 (1956) 109.
303 A.S. Bhaduri and P. Ray, Fresenius Z. Anal. Chem., 154 (1957) 103.
304 A.K. Chakraburtty, J. Xavier and P. Ray, Sci. Cult., 20 (1954) 146.
305 A.K. Chakraburtty, Proc. Ind. Sci. Congr. Abstr., 3 (1958) 149.
306 A.K. Chakraburtty, Proc. Symp. Coord. Chem., 3 (1960) 225.
307 D. Bandyopadhayay, J. Indian Chem. Soc., 33 (1956) 269, 276.
308 D. Bandyopadhayay, Fresenius Z. Anal. Chem., 155 (1957) 118.
309 D. Bandyopadhayay and P. Ray, J. Indian Chem. Soc., 33 (1956) 21, 65.
310 D. Bandyopadhayay and P. Ray, Fresenius Z. Anal. Chem., 155 (1957) 117.
311 D. Banerjea, Fresenius Z. Anal. Chem., 159 (1957) 123.
312 H.V. Weiss and M.G. Lai, Talanta, 8 (1961) 72.
313 N.S. Bhave and R.B. Kharat, J. Inorg. Nucl. Chem., 42 (1980) 977.