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Pseudo-halide Complexes of Transition Metals. Part I. Synthesis and Properties of Cobalt("), Nickel("), Copper("), and Zinc(") Derivatives

By B. R. Hollebone and R. S. Nyholm,* Department of Chemistry, University College, 20 Gordon Street, London WC1H 0AJ

A series of anionic four-co-ordinate complexes of bivalent cobalt, nickel, copper, and zinc have been prepared from a number of organic pseudo-halide anions, e.g. pentafluoro- and pentachloro-phenoxide, thioacetate, pentafluorobenzenethiolate, benzenethiolate, and (2,4,6-trichlorophenyl)- and (2-chlorophenyl)-carbodi-imide anions.

The complex anions were isolated as salts with a large cation. The physical properties of the compounds are reported, including magnetic moments, and u.v. and visible spectral data. The position of the ligands in both the spectrochemical and nephelauxetic series is compared with those of the simple halide ions. All the ligands show values of the parameter 10Dq larger than that for the three halide ions but smaller than for the NCO- or NCSions. The nephelauxetic B values show less regularity.

This is the first of two papers describing the preparation and physical properties of complexes of bivalent cobalt, nickel, copper, and zinc with various pseudo-halide ligands. We wished to synthesize the organic analogues of halide and pseudo-halide ions and to investigate the structure of their metal complexes. The ligands used [(I)-(VII)] have donor atoms (or groups) which are bivalent and also two-co-ordinate in the compounds studied here. One of the valencies is involved in bonding to an organic radical, the other being available for the formation of a covalent bond to a metal atom.



By the use of these ligands we have studied the effect of change in the electron-withdrawing power of substituents on the organic radical and therefore the effect of a change in the electronegativity of the donor atom on the nature of the ligand-metal bond. We wished to obtain chelate groups which are equivalent to two cishalide ions, and polydentate ligands which also incorporate other donor atoms.

This paper describes the preparation of the ligands and several of their transition-metal complexes; the magnetic and spectral properties of the complexes are described and used to infer their symmetries. In Part II, the nature of the ligand-metal bond is discussed and the symmetries of the complexes correlated with their spectral parameters.

RESULTS AND DISCUSSION

Ligands.—Three new types of ligands were examined and are considered in terms of their donor atoms.

Oxygen donor. Halogenated phenols were used because of their relatively high acidities without the interference of a second donor atom encountered in carboxylate complexes.¹ Phenoxides have been little used as ligands² although early transition-metal ions in high oxidation states form neutral complexes which are sensitive to oxygen and moisture.³ Anionic phenoxide complexes appear to be unknown. However, complete ring substitution by halogens not only blocks any oxidation via quinone formation but greatly increases the acidity, making salts of these ions much more stable to hydrolysis. The ions used in this work, pentafluoro-4 and pentachloro-phenoxide form air-stable, anionic transition-metal complexes and display chemical behaviour similar to halide ions.

Sulphur donor. Thiocarboxylates (III) and benzenethiolates [(V) and (VI)] were examined. Anionic thiol complexes are rare because they are often rapidly oxidized in air either in solution or in the solid state. Also, the thermodynamic stability of transition-metal sulphides is high compared with the stability of the ligand and the complexes decompose more or less rapidly even in the dark in inert atmospheres. An earlier report of the compound tetraphenylarsonium tetrakis(pentafluorothiophenoxo)cobaltate(II) noted its rapid oxidation but no physical data concerning the compound were given.5

The thiocarboxylates investigated were trifluorothioacetate (IV), complexes of which had not been reported previously, and thioacetate (III) itself. Benzenethiolates (VI) are more acidic than are the corresponding phenols; by use of pentafluorobenzenethiolate (V),⁶ it

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⁵ (a) W. Beck and K. Stetter, *Inorg. Nuclear Chem. Letters*, 1966, 2, 383; (b) W. Beck, W. P. Fehlhammer, K. H. Stetter, and

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 ⁶ J. Burdon, D. J. Gilman, C. R. Patrick, M. Stacey, and J. C. Tatlow, Nature, 1960, 186, 231.

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¹ J. G. Bergman and F. A. Cotton, Inorg. Chem., 1966, 5, 1420.

 ² C. K. Jørgensen, 'Inorganic Complexes,' Academic Press, New York, 1963, p. 108.
 ³ R. Masthoff, H. Kohler, H. Boland, and F. Schmeil, Z.

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is possible to prepare anionic complexes which are stable to hydrolysis.

Di-imide donor. The most characteristic feature of pseudo-halide ions such as cyanate, and thio- and selenocyanate is a π -bond system extending over all three atoms which results in a very stable anionic form.⁷ In each case there is a terminal group VI atom. Replacement of this atom by an imide group yields a carbodiimide ion (VIII),⁸ which retains the highly stable bonding system of the pseudo-halides. These carbodi-imides have not been used previously as ligands although their parent acids and alkali salts are well known.^{8a} The chemistry of the alkyl derivatives is dominated by the susceptibility of the cyanide group to electrophilic attack; they polymerize readily on heating or in strongly acidic or basic media. However, phenylcarbodi-imide and its halogensubstituted derivatives are thermodynamically stable under normal conditions and are sufficiently acidic to form stable salts. We have used (2-chlorophenyl)-(VIII)⁹ and (2,4,6-trichlorophenyl)-carbodi-imide (VII) anions.

Complexes.—The reaction of the silver or thallium(I) salts of the ligand with tetrahalogenocomplexes of the bivalent metal ions, in non-aqueous solvents, yields fully substituted four-co-ordinate complexes in most cases. The reaction can be written:

$[A^+]_2MX_4 + 4TlL \longrightarrow [A^+]_2ML_4 + 4TlX$

where $[A^+]$ is a large organic cation, M is the bivalent metal ion, and L is the ligand.

In spite of the insolubility of the silver or thallium(I) salts of most ligands used in the non-aqueous solvents, the ligand exchange was complete in each case and no byproducts containing halide ions were observed. Presumably the halide of thallium(I) is even less soluble than its ligand salt. Depending on the organic cation used, the anionic metal complexes are soluble in organic solvents such as acetone and nitromethane. Spectral studies of the halogeno-complexes show that solvolysis occurs to varying degrees; the pseudo-halogen complexes studied here display similar behaviour. However, solution in dry dichloromethane is said ¹⁰ to cause little or no change in the spectrum from that observed in the solid state. The spectra listed in Table 1 were recorded when possible for solutions in this solvent or in dry acetone in which these effects are also small. When possible the first charge-transfer band of the complex, as distinct from ligand internal transitions, has also been recorded. The analogous zinc compounds, in which this transition does not occur, were used to determine the

⁷ E. L. Wagner, J. Chem. Phys., 1965, **43**, 2728. ⁸ (a) P. A. S. Smith, 'Open Chain Nitrogen Compounds,' Benjamin, New York, 1965, p. 251; (b) F. Baum, Ber., 1908, **41**, 523. ⁹ (a) D. W. Browne and G. M. Dyson, J. Chem. Soc., 1931,

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TABLE 1 Electronic spectra of metal complexes in solution (CH CI)

	(0112012/	
		First charge- transfer
Complex	Ligand-field bands (cm ⁻¹)*	band (cm ⁻¹) *
$[Ph_4As]_2[Co(pfp)_4]$	6850(57), 16,530(350), 17,860(23)	
$[Ph_4As]_2[Co(pcp)_4]$	6700(33), 15,380(280), 16,250(250)	
$[Ph_4As]_2[Co(tac)_4]$	6700(60), 14,650(380), 15,260(360)	30,300(2600)
$[\mathrm{Bu}_4\mathrm{N}]_2[\mathrm{Co}(\mathrm{fbt})_4]$	6290(65), 13,075(457), 15,150(400), 17,800(300)	27,200(3000)
$[\operatorname{Bu}_4\mathrm{N}]_2[\operatorname{Co}(\mathrm{bt})_4]$	6700(60), 13,500(425), 15,500(475), 16,000(300)	23,500(3000)
$[Et_4N]_2[Co(Cl_3cd)_4]$	7450(230), 15,800 (1400)	32,000(6000)
$[Ph_4As]_2[Co(Clcd)_4]$	7250(200), 15,400(1200), 16,700(850)	25,400(4000)
[Ni(pfp) ₂]	8700(2), 16,250(5)	
[Ph ₃ MeAs] ₂ [Ni(pcp) ₄]	8700(13), 14,100(30)	31,800(5000)
[Ph ₃ MeAs] ₂ [Ni(fbt) ₄]		33,900(3300)
$[Et_4N]_2[Ni(Cl_3cd)_4]$	9750(125), 14,900(110), 16,400(130)	23,200(2000)
$[Ph_4As]_2[Ni(Clcd)_4]$	12,600(125), 14,900(150), 16,400(165)	22,200(3000)
$[Et_4N]_2[Cu(pfp)_4]$	12,375(90), 14,675(140)	25,000(3300)
$[Et_4N]_2[Cu(pcp)_4]$	11,100(160), 13,075(140)	22,000(3300)
$[Et_4N]_2[Cu(Cl_3cd)_4]$		17,800(630)
Ph.As] [Cu(Clcd).]		17.000(2500)

 $[Ph_4As]_2[Cu(Clcd)_4]$

Ligands abbreviations:

pfp-, pentafluorophenoxide; pcp-, pentachlorophenoxide; tac-, thioacetate; fbt-, pentafluorobenzenethiolate; bt-, benzenthiolate; Cl₃cd-, (2,4,6-trichlorophenyl)carbodi-imide; Clcd-, (2-chlorophenyl)carbodi-imide.

* ε in parentheses.

positions and intensities of the internal transitions of the complexed ligands. This enabled the position of the ligand-metal band in the other complexes to be unambiguously assigned in most cases.

The analysis ¹¹ of the spectra of the various complexes, taking account of second-order interactions between like ligand-field terms and of spin-orbit coupling where necessary, yields the values of ligand-field and interelectron repulsion parameters given in Table 2. The room temperature magnetic moments are also included (Table 3). The stereochemistries of the complexes can be inferred from a comparison of their spectral and magnetic properties with those of similar compounds having known structures. The different possible symmetries of cobalt and nickel complexes are characterized by well separated ranges of values of 10Dq and μ_{eff} except where gross, low-symmetry distortions occur.¹² The symmetries of copper complexes cannot be found this way since 10Dq and μ_{eff} values are insensitive to structural changes.^{12d} However, the position of the complex charge-transfer spectrum can be used to differentiate between four- and six-co-ordination of the copper(II)

 ⁽a) D. W. Browne and G. M. Dyson, J. Chem. 306., 1931, 3285; (b) F. Kurzer, J. Chem. Soc., 1949, 3033; (c) S. E. Forman, C. A. Erickson, and H. Adelman, J. Org. Chem., 1963, 28, 2653.
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 (b) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, J. Amer. Chem. Soc. 1061, 29, 4600. Chem. Soc., 1961, 83, 4690; (c) L. L. Katzin, J. Chem. Phys., 1962, 36, 3034.

¹¹ B. N. Figgis, 'Introduction to Ligand Fields,' Interscience, New York, 1966.

¹² (a) J. Lewis, Sci. Progr., 1963, 50, 450; (b) R. L. Carlin, 'Transition Metal Chemistry,' vol. 1, Edward Arnold, London, 1951, p. 1; (c) L. Sacconi, 'Transition Metal Chemistry' vol. IV, 1968, p. 199; (d) R. D. Willet, J. Chem. Phys., 1964, 41, 2243.

ion. These bands occur in the near-i.r. and visible regions with four-co-ordinate copper(II) compounds but appear in six-co-ordinate complexes in the u.v. region.

The individual complexes are conveniently discussed in terms of the transition-metal ion.

Cobalt complexes. Both tetrakis(pentafluorophenoxo)cobaltate(II) and tetrakis(pentachlorophenoxo)cobaltate-(II) are blue complexes which are stable in air when isolated with large organic cations. The assignment of the

TABLE	2
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Spectral parameters of the complexes				
	10Dq	B		
Complex	(cm ⁻¹)	(cm-1)		
$[Ph_4As]_2[Co(pfp)_4]$	3920	770		
$[Ph_4As]_2[Co(pcp)_4]$	3850	715		
$[Ph_4As]_2[Co(tac)_4]$	3870	645		
$[Bu_4N]_2[Co(fbt)_4]$	3660	631		
$[Bu_4N]_2[Co(bt)_4]$	3870	600		
$[Et_4N]_2[Co(Cl_3Cd)_4]$	4310	685		
$[Ph_4As]_2[Co(Clcd)_4]$	4210	705		
[Ni(pfp) ₂]	10,100	800		
$[Ph_{3}MeAs]_{2}[Ni(pcp)_{4}]$	4300	695		
[Ph ₃ MeAs] ₂ [Ni(fbt) ₄]				
$[Et_4N]_2[Ni(Cl_3Cd)_4]$	5150	795		
$[Ph_4As]_2[Ni(Clcd)_4]$	6700	710		
$[Et_4N]_2[Cu(pfp)_4]$	11,600			
$[Et_4N]_2[Cu(pcp)_4]$	10,300			
$[Et_4N]_2[Cu(Cl_3Cd)_4]$				
[Ph ₄ As] ₉ [Cu(Clcd) ₄]				

TABLE 3

Room-temperature magnetic data for the metal complexes *

	χ _M (corr.)	Diamagnetic	
	(× 106	correction	μ_{eff}
Complex	c.g.s.u.)	($ imes$ 10 ⁶ c.g.s.u.)	(BM)
$[Ph_4As]_2[Co(pfp)_4]$	9400	800	4.75
$[Ph_4As]_2[Co(pcp)_4]$	9500	1050	4.76
$[Ph_4As]_2[Co(tac)_4]$	9315	655	4.70
$[Ph_4As]_2[Co(fbt)_4]$	8830	890	4 ∙69
$[Bu_4N]_2[Co(bt)_4]$	7960	710	4.42
$[Et_4N]_2[Co(Cl_3cd)_4]$	7900	900	4.42
$[Ph_4As][Co(Clcd)_4]$	8380	730	4.48
[Ni(pfp) ₂]	4570	165	3.28
$[Et_4N]_2[Ni(pcp)_4]$	5640	790	3.65
$[Bu_4N]_2[Ni(fbt)_4]$	†		Ť
$[Et_4N][Ni(Cl_3cd)_4]$	2550	900	2.65
$[Ph_4As][Ni(Clcd)_4]$	3500	750	2.90
$[Et_4N]_2[Cu(pfp)_4]$	1500	540	1.89
$[Et_4N]_2[Cu(pcp)_4]$	1710	790	2.00
$[Et_4N]_2[Cu(Cl_3cd)_4]$	2000	900	1.94
$[Ph_4As]_2[Cu(Clcd)_4]$	1470	730	1.88

* These data are uncorrected for temperature-independent paramagnetism. The diamagnetic corrections were obtained both from measurement of the susceptibility of the analogous zinc(II) compounds and of thallium(I) or silver salts of the ligands. The values of the corrections ($\times 10^{-6}$ c.g.s.u.) used were: [Ph₄As]⁺, 218; [Bu₄N]⁺, 207; [Et₄N]⁺, 110; Zn²⁺, 12. The mean values for anionic ligands are pfp⁻, 70; pcp-, 140; fbt, 95; bt-, 68; tac-, 39; Clcd, 58; Cl₃cd, 106. † Diamagnetic.

6800 and 16,000 cm⁻¹ bands as ${}^4\!A_2 \rightarrow {}^4\!T_1(F)$ and ${}^4\!A_2 \rightarrow$ ${}^{4}T_{1}(P)$ respectively yields values of 10Dq suggesting regular tetrahedral symmetry in both cases. This is supported by the values of the magnetic moments for both complexes.

¹³ J. L. Danziger, J. Amer. Chem. Soc., 1902, 24, 578.
¹⁴ (a) N. Sheppard, Trans. Faraday Soc., 1949, 45, 693;
(b) R. S. Rasmussen and P. R. Brattain, 'The Chemistry of Penicillin,' Princeton University Press, 1949, p. 104.

Trifluorothioacetate reacts with cobaltate(II) to give cobalt sulphide. The tetrakis(thioacetato)cobaltate(II) complex, which occurs as a green solid, was first prepared as a water-insoluble precipitate ⁵ and was initially formulated as an ammonium double salt.¹³ The i.r. spectrum has a sharp, intense band at 1615 cm⁻¹ assigned to C=O¹⁴ indicating that the oxygen takes little part in ligand-metal bonding.

Pentafluorobenzenethiolate and benzenethiolate both form well characterized four-co-ordinate cobalt(II) complexes. They are isolated as green solids stable in dry air. The spectra of the phenoxide, thiophenoxide, and pentafluorophenoxide cobalt(II) complexes indicate that all have regular tetrahedral symmetry; this is supported by the magnetic data. The compounds display chargetransfer bands in the visible to near u.v. region resulting in their characteristic green colour.

Both (2,4,6-trichlorophenyl)- and (2-chlorophenyl)carbodi-imide form blue-green four-co-ordinate complexes by metathetical reaction; these complexes are air stable when precipitated with large cations. Assignment of their spectra again indicates tetrahedral symmetry for both complexes and this is supported by the magnetic moment value. The values of 10Dq and μ_{eff} are similar to those observed with the four-coordinate cobalt(II) pseudohalide complexes.¹⁵

Nickel complexes. Attempts to prepare a tetrakis-(pentafluorophenoxo)nickelate(II) complex were unsuccessful. In spite of the use of the metathetical reaction described and recovery of four moles of thallium-(I) chloride, the only nickel-containing material which could be isolated was the binary salt, nickel pentafluorophenoxide as a light green, air-stable solid. The magnetic moment and ligand-field parameter values (the latter obtained by assigning the 8700 and 16,000 cm⁻¹ bands as ${}^{\mathbf{3}}\!A_{\mathbf{2}} \rightarrow T_{\mathbf{2}}(F) \text{ and } {}^{\mathbf{3}}\!A_{\mathbf{2}} \rightarrow T_{\mathbf{1}}(F) \text{ respectively}$, indicate that the nickel ion is octahedrally co-ordinated. The structure of the solid, which contained no solvent, is not obvious. On the other hand, tetrakis(pentachlorophenoxo)nickelate can be prepared and when isolated with a large cation is an air-stable, blue-green solid. The value of 10Dq obtained by assigning the 8700 and 1400 cm⁻¹ bands as ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(F)$ and ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ respectively and allowing for a spin-orbit coupling splitting of the ground term with $\lambda - 275$ cm⁻¹,¹⁶ indicates tetrahedral symmetry. These transitions are an order of magnitude more intense than those observed in nickel bis(pentafluorophenoxide) and, together with the magnetic moment, indicate tetrahedral symmetry. The compound is green because an intraligand transition is affected by a strong mesomeric effect and this results in the band appearing <30,000 cm⁻¹; there is also a broadening due to mixing with ligand-metal charge transfer band. The tail of this absorption extends well into the visible region.

As observed with cobalt, trifluorothioacetate reacts nickel(11) producing nickel sulphide. The with

P. Day, Inorg. Chem., 1966, 5, 1619.
 H. A. Weakliem, J. Chem. Phys., 1962, 36, 2117.

chemistry of nickel(II) with the other thiol ligands is more complicated. The tetrakis(pentafluorobenzenethiolato)nickelate(II) complex can be prepared as a green-brown air unstable solid when isolated with a large cation. No ligand-field transitions are observable as the spectrum is dominated by charge-transfer bands. The complex is diamagnetic and hence is presumably square planar.

Although the metathetical reaction is predisposed towards the formation of four-co-ordinate complexes, these could not be isolated from the reaction of tetrachloronickelate(II) with thallium(I) thioacetate or benzenethiolate. The products in both cases were dark brown oils, soluble in organic solvents; reproducible analyses on these products could not be obtained. Polymeric nickel mercaptides, soluble in non-polar solvents, are well known and these oily residues are probably such mixtures.¹⁷

The halogen-substituted phenylcarbodi-imides both form four-co-ordinate air-stable compounds with nickel-(II) when isolated with large cations. However, the stereochemistry of the two complexes are difficult to assign with certainty from the spectral and magnetic parameters. The (2,4,6-trichlorophenyl)carbodi-imide complex is blue-green in solution and is isolated as a yellow-green solid. Intense charge-transfer bands appear >20,000 cm⁻¹ in the spectrum. Assignment of the 10,000 and 16,000 cm⁻¹ bands as ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}$ and ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ respectively yields values of 10Dq and B which imply tetrahedral symmetry about the nickel ion in solution. The solid-state magnetic moment however is anomalously low which could indicate that orbital angular momentum has been quenched by distortion of the complex towards a square plane. This behaviour is reminiscent of the tetrathiocyanatonickelate(II) complex ¹⁸ which can be isolated from solution in either a blue tetrahedral form or yellow-green square planar form, depending on temperature and cation size. The latter form has μ_{eff} 3.3 BM, and is thought to have a nickel-sulphur bond between adjacent anions.

The nickel complex with (2-chlorophenyl)carbodiimide is isolated only with difficulty by use of tetraphenylarsonium ion as the cation. Charge-transfer bands dominate the spectrum >18,000 cm⁻¹ and a long tail persists through the visible region into the i.r. The lowest energy band, at 12,000 cm⁻¹, is very broad and substantially more intense than usually observed ¹⁹ for tetrahedral nickel complexes. Assignment of the 12,000 and 16,000 cm⁻¹ bands as ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}$ and ${}^{3}T_{1}(F) \rightarrow$ ${}^{3}T_{1}(P)$ respectively leads to a very high value of 10Dqfor a tetrahedral nickel(II) complex. The magnetic moment is abnormally low and together with the spectral data indicates a strong distortion from a regular tetrahedron.^{12c}) The complex is difficult to obtain solventfree; while this accounts for poor and analytical figures, it may indicate that the nickel is tending towards a five-co-ordinate species, perhaps similar to the pentacyanonickelate(II) complex.²⁰

Copper complexes. Both pentafluoro- and pentachloro-phenoxide form four-co-ordinate complexes with copper(II) which are strongly coloured and air stable. The assignment of the 12,000 and 14,000 cm⁻¹ bands in the former and the 11,000 and $13,000 \text{ cm}^{-1}$ bands in the latter as ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ and ${}^{2}B_{2} \rightarrow {}^{2}A_{1}$ respectively,²¹ give values of 10Dq which are normal for oxygen donorligands on copper(II). A spin-orbit coupling of $\lambda - 800$ cm⁻¹ is used in the analysis of these data. The magnetic moments are also within the expected region for magnetically dilute copper(II) complexes.²² However, the first ligand-metal charge-transfer bands occur between 22,000 and 25,000 cm⁻¹ and both complexes are expected to have the same distorted tetrahedral symmetry as the analogous tetrachlorocuprate(II) complex.²²

Copper(II) is immediately reduced to copper(I) by all the thiol ligands.²³ However, both (halogenophenyl)carbodi-imide ligands form very dark purple-blue airstable four-co-ordinate complexes which are crystalline when isolated with large cations. Their spectra consist of a single, broad, featureless band of high intensity near 17,000 cm⁻¹. It must be assumed that both ligand-field transitions²⁴ and ligand-metal charge-transfer are occurring in the same region and cannot be separated. The magnetic moment in both complexes is normal and the symmetry can only be postulated as a distorted tetrahedron, usually found for four-co-ordinate cuprates(II).

Zinc complexes. Apart from trifluorothioacetic acid, which forms zinc sulphide, all the ligands gave white, four-co-ordinate anions isolated as solids with a suitable large cation. The symmetry in each case is probably tetrahedral by analogy with the structure of tetrachlorozincate(II).²⁵ The exception arose in the reaction of the tetrachlorozincate(II) with thallium benzenethiolate when the only zinc-containing derivative was the binary zinc compound, zinc benzenethiolate. This light-yellow solid is relatively stable in air compared with the anionic complexes of this ligand and is soluble in nonpolar solvents. In acetone the molecular weight is that of the undissociated compound. The large chemical shift to low field of the ortho-protons, τ 1.14 relative to their position in the parent acid τ 3.83,²⁶ indicates that the ligand is strongly bound to the metal atom. The structure of this well known compound has not been investigated but is probably similar to that of the analogous mercury mercaptides 27 with an S-Hg-S angle of 180°.

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 ²⁵ B. Morosin and E. C. Lingafelter, Acta Cryst., 1959, 12, 611.
 ²⁶ S. H. Marcus and S. I. Miller, J. Phys. Chem., 1964, 68, 331.
 ²⁷ D. C. Bradley and N. R. Kunchur, J. Chem. Phys., 1964, 40, 2258.

P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, J. Amer. Chem. Soc., 1965, 87, 5251.
 ¹⁸ D. Forster and D. M. L. Goodgame, Inorg. Chem., 1965, 4,

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¹⁹ N. K. Hamer, Mol. Phys., 1963, 6, 257.

²⁰ K. N. Raymond and F. Basolo, Inorg. Chem., 1966, 5, 949.

²¹ J. Ferguson, J. Chem. Phys., 1964, 40, 3406.

Placing these ligands in the spectrochemical series, the order of decreasing values of 10Dq in cobaltate(II) complexes is: $-NCO > -NCS > Cl_3cd^- > Clcd^- > pfp^- \ge$ $tac^- \ge pcp^- \ge bt^- > fbt^- > Cl^- > Br^- > I^-$.

In the nephelauxetic series the order of decreasing Bvalues observed in cobaltate(II) complexes is: pfp > $Cl^- > -NCO > pcp^- > Clcd^- > -NCSe > Cl_3cd^- >$ $-NCS > Br^{-} > I^{-} > tac^{-} > fbt^{-} > bt^{-}$.

The theoretical basis of the ligand-field splitting is still not sufficiently understood well for the ligand positions to be rationalized in the spectrochemical series. The nephelauxetic series has been associated with the covalence of the metal-ligand bond and the decreasing values of B tend to follow the donor atom electronegativities.²⁸ However, the unexpectedly high positions of ligands such as selenocyanate and 2-(chlorophenyl)carbodiimide presumably reflect the influence of π -donation to the metal by ligands with low-lying conjugated π systems involving the donor atom and will be discussed in the following paper.

From the distribution of ligands in these two series it is clear that changing the electronegativity of the organic substituent has an observable effect on the properties of the ligand-metal bond. All the ligands form complexes which are very similar in most cases to those formed by the halide ions nearest to them in the nephelauxetic series. The complexes are prepared under similar chemical conditions, are hydrolysed by protonic solvents and are soluble in a wide range of non-polar media. For these reasons, in addition to cyanate, thiocyanate, selenocyanate, and azide ions, all the ligands described in this paper will be referred to as pseudohalides in Part II of this series.

These monodentate ligands now open a route to polydentate pseudo-halide ligands by linking together of the organic radicals.

EXPERIMENTAL

Preparation of Ligands.---The parent acids were usually available and the thallium(I) or silver salts were prepared from these.

Thallium(1) pentafluorophenoxide. This was prepared from pentafluorophenol in aqueous ammonia mixed with one equivalent of aqueous thallium(I) acetate after concentration of the solution and cooling.

Thallium pentachlorophenoxide. This was prepared from pentachlorophenol in aqueous sodium hydroxide with one equivalent of aqueous thallium(I) acetate as a finely divided precipitate.

Thallium(I) and silver salts react with thiocarboxylates to give the sulphide. The potassium salts of these ligands were prepared.

Potassium trifluorothioacetate. Trifluorothioacetic acid was prepared as for thioacetic acid,29 by distillation from an equimolar mixture of trifluoroacetic acid and thiobenzoic acid. It was dissolved slowly in an ice-cold solution of

²⁸ C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, London, 1962, p. 138.
²⁹ I. A. M. Ford and S. A. M. Thompson, *Nature*, 1960, 185, 96.

equimolar potassium hydroxide and the water removed by freeze drying to give a white crystalline hygroscopic solid.

Potassium thioacetate. Thioacetic acid was dissolved slowly in ice-cold aqueous potassium hydroxide to give a yellow solution which was evaporated to give the compound as a white unstable solid.

Thallium pentafluorobenzenethiolate. Pentafluorobenzenethiol was added to an equimolar solution of thallium(I) acetate in methanol. The compound was deposited immediately as a light yellow solid which was repeatedly washed with methanol.

Thallium(I) benzenethiolate. Benzenethiol in methanol with methanolic thallous acetate immediately gave the required compound as a yellow precipitate.

Carbodi-imides. Reported attempts using weakly basic amines including those heavily substituted by halogens have been unsuccessful.³⁰ We have used the substitution of an amine proton by benzoyl thiocyanate, prepared in situ from benzoyl chloride and ammonium thiocyanate in acetone, followed by hydrolysis with boiling aqueous sodium hydroxide.³¹ The resulting chlorophenylthiourea was then desulphurized with boiling basic lead acetate to the carbodi-imide.⁹ These reactions can be represented;

$$C_6H_xCl_{(5-x)}NH_2 + PhCONCS \longrightarrow C_6H_xCl_{(5-x)}NH \cdot CS \cdot NH \cdot COPh$$

$$\begin{array}{c} \mathbf{C_6H_xCl_{(5-x)}NH\cdot CS\cdot NH\cdot COPh} + \operatorname{NaOH} \longrightarrow \\ \mathbf{C_6H_xCl_{(5-x)}NH\cdot CS\cdot NH_2} + \operatorname{NaCO_2Ph} \end{array}$$

$$\begin{array}{c} \mathbf{C_6H_xCl_{(5-x)}NH\cdot CS\cdot NH_2 + Pb(O_2Me)_2 + 2NaOH \longrightarrow} \\ \mathbf{C_6H_xCl_{(5-x)}Cl_xNH\cdot CN + 2NaO_2CMe + PbS} \end{array}$$

Both (2-chlorophenyl)- and (2,4,6-trichlorophenyl)-carbodiimide prepared by this method were obtained, in 80 to 90% yields, as white, air stable solids.

Silver (2-chlorophenyl)carbodi-imide and Silver (2,4,6-trichlorophenyl)carbodi-imide. These were prepared by mixing equivalent quantities of silver perchlorate with the protonated ligand in methanol as flocculent white precipitates.

Attempted syntheses of more heavily chlorinated and of fluorinated ligands were unsuccessful, red tarry byproducts being formed.

Preparation of the Complexes.—These were all prepared by metathetical reaction, with vigorous stirring at room temperature, of the tetrahalometalate(II) (1 mole) dissolved in a dried non aqueous solvent (usually acetonitrile) with the finely ground thallium(I) or silver salt of the ligand (4 moles).The filtered solution was evaporated in vacuo to a small volume and in most cases the complexes isolated by addition of dried ether or light petroleum. The thiolate complexes were prepared under nitrogen. It was difficult to purify some of the complexes particularly those of nickel, in which the symmetry is uncertain. The following complexes were prepared: tetraphenylarsonium tetrakis(pentafluorophenoxo)cobaltate (II), blue, from acetone with ether (Found: C, 56·1; H, 3·0; Co, 3·9. C₇₂H₄₀O₄F₂₀As₂Co requires C, 55.5; H, 2.6; Co, 3.8%); tetraphenylarsonium tetrakis(pentachlorophenoxo)cobaltate (II), blue, from acetonitrile with ether (Found: C, 45.7; H, 2.2; Co, 3.1. C72H40O4Cl20As2Co requires C, 45.5; H, 2.1; Co, 3.1%); tetraphenylarsonium tetrakis(thioacetato)cobaltate(II), blue-

³⁰ G. M. Dyson and H. George, J. Chem. Soc., 1924, 1702.

³¹ R. L. Frank and P. V. Smith, Org. Synth., Coll. Vol. II, 1955, p. 735.

green from water (Found: C, 59.2; H, 4.6; Co, 5.2. $C_{56}H_{52}O_4S_4As_2Co$ requires C, 59.7; H, 4.6; Co, 5.2%); tetrakis(pentafluorobenzenethiolato)*tetrabutylammonium* cobaltate(II), bright green from acetone with ether (Found: C, 50.5; H, 5.4; Co, 4.3. C₅₈H₉₂F₂₀N₂S₄Co requires C, 51.1; H, 5.8; Co, 4.3%); tetrabutylammonium tetrakis-(benzenethiolato)cobaltate(II), bright green from acetone with ether (Found: C, 69.1; H, 9.2; Co, 5.9. C₅₈H₉₂N₂S₄Co requires C, 69.2; H, 9.4; Co, 5.9%); tetraethylammonium tetrakis[(2,4,6-trichlorophenyl)carbodi-imidato]cobaltate(II) blue from dichloromethane with light petroleum (Found: C, 43.8; H, 4.0; N, 11.1. C₄₄H₄₈N₁₀Cl₁₂Co requires C, 43.9; H, 4.0; N, 11.6%; tetraphenylarsonium tetrakis[(2-chlorophenyl)carbodi-imidato]cobaltate(11), blue green from acetonitrile with ether (Found: C, 63.7; H, 4.1; Co, 4.1. C₂₈H₅₆N₈Cl₄As₂Co requires C, 63.8; H, 4.1; Co, 4.15%); nickel pentafluorophenoxide, light green from acetonitrile with ether (Found: C, 34.7; H, 0.5; Ni, 13.5. C₁₂F₁₀O₂Ni requires C, 33.9; H, 0.0; Ni, 13.9%) (it was difficult to remove traces of tetraphenylarsonium pentafluorophenoxide); triphenylmethylarsonium tetrakis(pentachlorophenoxo)nickelate(11), green from acetonitrile with ether (Found: C, 43.2; H, 2.1. C₆₂H₃₆Cl₂₀O₄As₂Ni requires C, 42.3; H, 2.0%); triphenylmethylarsonium tetrakis(pentafluorobenzenethiolato)nickelate(II), dark green-brown from acetone with ether (Found: C, 50.6; H, 2.6; Ni, 4.2. C₆₂H₃₆F₂₀As₂S₄Ni requires C, 49.6; H, 2.5; Ni, 4.2%); tetraethylammonium tetrakis[(2,4,6-trichlorophenyl)carbodi-imidato]nickelate(II), green from dichloromethane with light petroleum ether (Found: C, 42.1; H, 4.8; N, 11.0. C44H48N10Cl12Ni requires C, 43.9; H, 4.0; N, 11.6%); tetraphenylarsonium tetrakis[(2-chlorophenyl)carbodi-imidato]nickelate(II), brown,

tetrakis[(2-chlorophenyl)carbodi-imidato]nickelate(II), brown, amorphous, glassy solid from dichloromethane with light petroleum (Found: C, 61·0; H, 3·9; N, 6·9. $C_{76}H_{56}N_8Cl_4$ -AsNi requires C, 63·6; H, 3·9; N, 7·8%) (stoicheiometry not well defined and crystalline samples difficult to obtain); tetraethylammonium tetrakis(pentafluorophenoxo)cuprate(II), dark green from acetone with ether (Found: C, 45·7; H, 4·0; Cu, 6·1. $C_{40}H_{40}F_{20}O_4N_2Cu$ requires C, 45·5; H, 3·8; Cu, 6·1%); tetraethylammonium tetrakis(pentachlorophenoxo)-

cuprate(II), dark orange red from acetonitrile with ether (Found: C, 35.1; H, 3.4; Cu, 4.8. C40H40Cl20O4N2Cu requires C, 34.5; H, 3.1; Cu, 4.6%); tetraethylammonium tetrakis[(2,4,6-trichlorophenyl)carbodi-imidato]cuprate(II), blue from dichloromethane with light petroleum (Found: C, 43.8; H, 4.2; N, 11.2. C₄₄H₄₈N₁₀Cl₁₂Cu requires C, 43.7; H, 4.0; N, 11.6%); tetraphenylarsonium tetrakis[(2-chlorophenyl)carbodi-imidato]cuprate(II), dark blue from acetonitrile with ether (Found: C, 62.3; H, 4.0; Cu, 4.75. $C_{76}H_{56}N_8Cl_4As_2Cu$ requires C, 63.1; H, 4.0; Cu, 4.7%); tetraethylammonium tetrakis(pentafluorophenoxo)zincate(II), white, from nitromethane with ether (Found: C, 43.5; H, 4.4. $C_{40}H_{40}F_{20}O_4N_2Zn$ requires C, 45.3; H, 3.8%); tetraethylammonium tetrakis(pentachlorophenoxo)zincate(II), white from nitromethane with ether (Found: C, 35.1; H, 3.2. C40H40Cl20O4N2Zn requires C, 34.5; H, 3.1%) (compounds prepared in nitromethane generally showed spectroscopic evidence of solvolysis and poor analytical results 10); tetraphenylarsonium tetrakis(thioacetato)zincate(II), white, from ethanol with ether (Found: C, 59.5; H, 4.6. C₅₆H₅₂-As₂O₄S₄Zn requires C, 59.5; H, 4.6%); tetrabutylammonium tetrakis(pentafluorobenzenethiolato)zincate(II), white from acetonitrile with ether (Found: C, 49.9; H, 5.7. C₅₈H₇₂N₂-F20S4Zn requires C, 50.0; H, 5.4%); zinc benzenethiolate, light yellow from acetone with ether [Found: C, 51.7; H, 4.0%; M (acetone) 272. $C_{12}H_{10}S_2Zn$ requires C, 51.4; H, 3.6%; M 281); tetraethylammonium tetrakis[(2,4,6-trichlorophenyl)carbodi-imidato]zincate(11), white, from dichloromethane (Found: C, 43.7; H, 4.5; N, 11.7. $C_{44}H_{48}$ - $N_{10}Cl_{12}Zn$ requires C, 43.7; H, 4.0; N, 11.6%; tetraphenylarsonium tetrakis[(2-chlorophenyl)carbodi-imidato]zincate(II), light yellow from acetonitrile with ether (Found: C, 64.0; H, 4.1. C₇₆H₅₆N₈Cl₄As₂Zn requires C, 63.1; H, 4.0%).

Physical Measurements.—Spectra were recorded on a Cary 14 spectrophotometer (2500—200 nm). Room-temperature magnetic moments were made by the Gouy method.³²

[0/544 Received, April 6th, 1970]

³² B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry,' Interscience, New York, 1964, 400.