Ionic Complexes from Cobalt and Zinc Halides with Pyridine *N*-Oxide and Trimethylamine Oxide*

Songchun Jin, Mark Nieuwenhuyzen and Cuthbert J. Wilkins
Chemistry Department, University of Canterbury, Christchurch, New Zealand

The range of ionic complexes obtainable from cobalt and zinc iodides with pyridine *N*-oxide (pyo) and trimethylamine oxide has been surveyed. The crystal structures of $[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$, $[Co(pyo)_6]^{2+}2I^-$, $[Co(Me_3NO)_4]^{2+}2I^-$ and $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$ have been determined by X-ray analysis. There is an isomorphous series constituted by $[Co(pyo)_6]^{2+}[CoX_4]^{2-}$ (X = Cl, Br or I) but the iodide decomposes to $[Co(pyo)_6]^{2+}2I^-$ in solution. Zinc gives four-co-ordinate molecular complexes $[Zn(pyo)_2X_2]$ preferentially. With trimethylamine oxide the cobalt co-ordination is also limited to four, as in $[Co(Me_3NO)_4]^{2+}2I^-$. The steric restriction here is from $CH_3\cdots O$ approaches. Spectroscopic evidence on $[Co(Me_3NO)_3I]^+I^-$, which is subject to ligand redistribution in solution, confirms its structure. Pyridine *N*-oxide differs from Me_3NO in the preferential formation of a mixed-ligand anion, as in the isomorphous salts $[NEt_4]^+[Co(pyo)I_3]^-$ and $[NEt_4]^+[Zn(pyo)I_3]^-$, and in $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$. In the crystal of the last compound the polarity of the anions leads to their packing into double layers.

The behaviour of polar covalent halides of divalent metals towards monodentate oxo ligands is determined largely by the competition between ligand and halide and, with the ligand in sufficient excess, ionic derivatives can often be obtained.[1–4] With cobalt chloride and bromide, MX_4^{2-} anion formation is considered likely.[5] The response of metal iodides in general is more varied, since iodide may be set free through the relative weakness of the M–I bond. This happens in the compounds $[Co(Me_2SO)_6]^{2+}2I^-$ (ref. 1) and $[Co(Me_3NO)_4]^{2+}2I^-$.[3] Then too, besides a mixed-ligand cation proposed (somewhat speculatively) for $[Co(Me_3NO)_3I]^+I^-$,[6] an example of a mixed-ligand anion has recently been found through an X-ray structure determination on the compound $[Fe(thf)_6]^{2+}2[Fe(thf)I_3]^-\cdot thf$,[7] which is formed between iron(II) iodide and tetrahydrofuran (thf).

Electronic spectra show that the iodide derivatives can be particularly sensitive to solvent changes and to addition of iodide or free ligand.[3,8,9] Moreover, the molecular cobalt halide complexes $[Co(Me_3NO)_2X_2]$ with trimethylamine oxide show conspicuous differences between their solid-state and solution spectra, which have remained largely unexplained. It was against this background that we have readdressed questions on the formation and structures of simple types of ionic products from cobalt and zinc iodides with Me_3NO and pyridine *N*-oxide (pyo). Information has been obtained on the derivatives listed in Table 1.

Results and Discussion

Background to the Preparative Approach.—Cobalt chloride and bromide form well known derivatives with pyo,[10] for which the formulation $[Co(pyo)_6]^{2+}[CoX_4]^{2-}$ has been inferred, though not proven.[5] A different constitution had been suggested for the iodide.[6] It is now found that the three halide complexes are isomorphous (Table 2), and with a crystal structure determination on the chloride $[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$ **1**, the tetrahalide anion formulation is confirmed. The iodide $[Co(pyo)_6]^{2+}[CoI_4]^{2-}$ **1b** decomposes to $[Co(pyo)_6]^{2+}2I^-$ **2** on attempted recrystallisation. With the ionic iodide $[Co(Me_3NO)_4]^{2+}2I^-$ **3** having been identified much earlier,[3,11] a comparison of the cation structures in **2** and **3** was made to define the steric constraint preventing six-co-ordination in **3**.

Table 1 Ionic products from cobalt and zinc halides

Halide	L = pyo[a]	L = Me_3NO[b]
$CoCl_2$	**1** $[CoL_6]^{2+}[CoCl_4]^{2-}$[c,d]	
$CoBr_2$	**1a** $[CoL_6]^{2+}[CoBr_4]^{2-}$[c]	**3a** $[CoL_4]^{2+}2Br^-$[e]
CoI_2	**1b** $[CoL_6]^{2+}[CoI_4]^{2-}$[c]	**3** $[CoL_4]^{2+}2I^-$[d]
	2 $[CoL_6]^{2+}2I^-$[d]	**4** $[CoL_3I]^+I^-$
	5 $[NEt_4]^+[CoLI_3]^-$	**8**[f] $[CoL_2I_2]$
$ZnBr_2$	**1c** $[ZnL_6]^{2+}[ZnBr_4]^{2-}$[c]	
ZnI_2	**5a** $[NEt_4]^+[ZnLI_3]^-$[g]	**7** $[ZnL_4]^{2+}2I^-$
	6 $[ZnL_6]^{2+}2[ZnLI_3]^-$[d]	

[a] All zinc halides form $[Zn(pyo)_2X_2]$ molecular compounds. [b] Both cobalt and zinc halides form the $[M(Me_3NO)_2X_2]$ series. [c] Members of an isomorphous series, which also includes $[Zn(pyo)_6]^{2+}[ZnBr_4]^{2-}$. [d] X-Ray analysis made. [e] Isomorphous with the iodide **3**. [f] Molecular complex. [g] Isomorphous with compound **5**.

Table 2 *d* Values (Å) with relative intensities in parentheses for $[Co(pyo)_6]^{2+}$ $[CoX_4]^{2-}$ isomorphous series

X = Cl	X = Br	X = I
9.452(92)	9.676(15)	9.910(23)
7.396(100)	7.518(65)	7.662(37)
6.721(88)	6.850(100)	7.020(100)
5.817(29)	5.987(49)	6.195(21)
		6.032(16)
4.715(88)	4.824(44)	4.952(20)
3.929(24)	4.033(46)	4.170(30)
3.847(25)	3.950(27)	4.073(38)
3.753(24)	3.826(25)	3.955(15)
		3.847(20)
2.996(41)	3.140(25)	3.244(25)
	3.044(21)	3.126(26)

As to the Me_3NO series, CoI_2L_2, CoI_2L_3, CoI_2L_4, now confirmed as $[CoL_2I_2]$ **8**,[12] $[CoL_3I]^+I^-$ **4**, $[CoL_4]^{2+}2I^-$ **3**, it was necessary to establish first that the intermediate product **4** exists as a separate phase. The primary product having this composition, though consistently obtainable,[6,13] in finely divided form from sufficiently concentrated solutions, could not be recrystallised unchanged from more dilute solution because it disproportionated to $[Co(Me_3NO)_2I_2]$ **8** and $[Co(Me_3NO)_4]^{2+}2I^-$ **3**. Nevertheless its X-ray powder pattern and infrared and electronic spectra are all distinctive. The spectra point decisively to the suggested ionic formulation with the

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

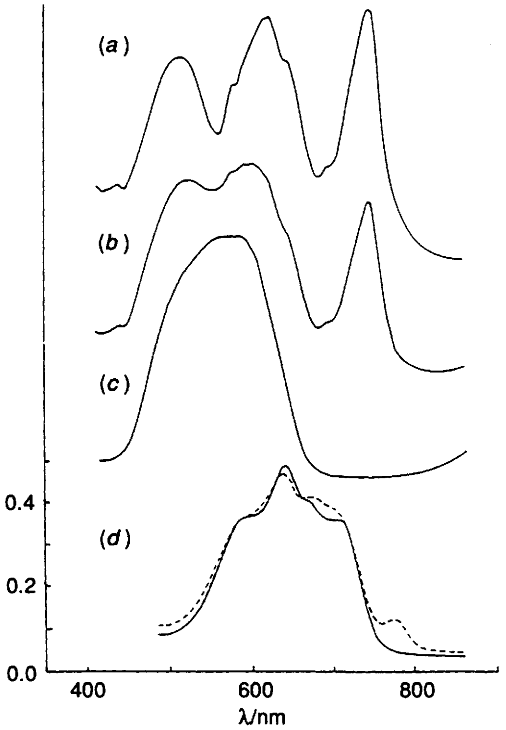


Fig. 1 The solid-state spectra of (*a*) $[Co(Me_3NO)_2I_2]$, (*b*) $[Co(Me_3NO)_3I]^+I^-$ and (*c*) $[Co(Me_3NO)_4]^{2+}2I^-$. The progressive change is evident, (*d*) with absorbance scale, shows solution spectra of $[Co(Me_3NO)_2I_2]$ (——, 1.36×10^{-3} mol dm^{-3} in dichloromethane; – – –, after addition of $NBu^n{}_4I$, 11.4×10^{-3} mol dm^{-3})

mixed-ligand cation $[Co(Me_3NO)_3I]^+$. Attempts to obtain a product with the mixed-ligand anion $[Co(Me_3NO)I_3]^-$ were not successful.

Comparison of Me_3NO and pyo co-ordination was useful here. There is evidence that Me_3NO is a stronger ligand than iodide,[3] so that additional ligand readily effects the conversion of complex **8** to **4** and **3**; but the replacement of ligand by iodide would be unlikely (quite apart from the need for a suitable counter cation to give a crystalline product). However, pyo is at least a weaker ligand than Me_3NO, as shown by the longer Zn–O, but shorter Zn–Cl, bond lengths in $[Zn(pyo)_2Cl_2]$[14] than in $[Zn(Me_3NO)_2Cl_2]$,[12] so that iodide should be better able to compete towards formation of an $[M(pyo)I_3]^-$ anion. Consistent with this, it proved possible to obtain the compounds $[NEt_4]^+[Co(pyo)I_3]^-$ **5** and $[NEt_4]^+[Zn(pyo)I_3]^-$ **5a**, and also $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$ **6**. A structure determination on the last gave precise information on this anion.

Range of Derivatives Obtainable.—With the range of derivatives as in Table 1 it is evident that the two metals show marked differences in their behaviour towards pyo. Cobalt forms $[Co(pyo)_6]^{2+}[CoX_4]^{2-}$ ionic complexes at the expense of molecular $[Co(pyo)_2X_2]$ derivatives. Zinc readily forms the latter type, and of the former only $[Zn(pyo)_6]^{2+}[ZnBr_4]^{2-}$ has been identified. Towards Me_3NO the behaviour is more uniform. Both metals give corresponding molecular adducts and ionic iodides $[M(Me_3NO)_4]^{2+}2I^-$.

While the differences towards pyo could arise in part from solubility differences they are consistent with recognised relationships. Zinc shows a generally greater preference for four-co-ordination (with $[CoX_4]^{2-}$ exceptional through halide polarisability[8,15]), and hence the predominance of its molecular complexes. The geometry of pyo makes it peculiarly suited to six-co-ordination, but the higher steric demand of Me_3NO blocks this for cobalt and zinc alike. At the same time the higher polarity of the N–O bond in the Me_3NO molecule than in pyo[16] means that there will be greater charge neutralisation (or transfer) per ligand at the metal centre; and co-ordination of only three or four Me_3NO molecules suffices to promote iodide ionisation. It is of interest that with a sufficient excess of ligand an ionic bromide $[Co(Me_3NO)_4]^{2+}2Br^-$ can also be crystallised. Its appearance gives point to Herlocker's observation[11] that excess of ligand shifts the solution spectrum of the molecular bromide towards that of the $[Co(Me_3NO)_4]^{2+}$ cation.

Electronic Spectra.—With the association of hard and soft (especially iodide) ligands in $[Co(Me_3NO)_2X_2]$ complexes the effective ligand field has lower symmetry. The ν_3 bands (500–800 nm) of the solid-state spectra become broader and generally more structured than those from $[Co(Me_3NO)_4]^{2+}$ or $[CoX_4]^{2-}$. In addition, there are the differences between the solid-state and solution spectra reported for the $[Co(Me_3NO)_2X_2]$ series,[3] and confirmed by the present observations. We add that $[Co(Me_3NO)_3I]^+I^-$ **4** shows the same behaviour. The solid (Fig. 1) shows maxima at 526, 597–606 (with shoulders at 581 and 645), and 750 nm, but in dichloromethane solution there is a single maximum at 637–640 (with shoulders at 560, 600–615, 670), and 713 nm. The solution spectrum of compound **4** shows features from complex **8** and *vice versa*; and this, in addition to the disproportionation of the compound into **8** and **3** points to ligand redistribution in solution. Addition of $NBu^n{}_4I$ to a solution of **8** produces a weak band at 779 nm (see Fig. 1), which matches the band of $[CoI_4]^{2-}$ at 783 nm.[8] As expected, disproportionation of **8** therefore gives (potentially) anionic species as well as the $[Co(Me_3NO)_3I]^+$ cation. Besides ligand redistribution, any dissociation of the Co–I bond, or variation in bond angles at cobalt,[12] could be expected to contribute to spectral differences in solution.

As regards the constitution of $[Co(Me_3NO)_3I]^+I^-$ **4** the solid-state spectra show a progression through the series **8**, **4**, **3**, which indicates an intermediate co-ordination environment in **4** (Fig. 1). It will be seen that both **4** and **8** show a rather sharp component at 750 nm. This band seems peculiar to the crystalline iodides, and its presence in the spectrum of **4** suggests this compound also contains a Co–I bond within a tetrahedral environment.

As to pyo complexes, the maxima in the ν_3 tetrahedral bands of the solid-state spectra from the $[Co(pyo)_6]^{2+}[CoX_4]^{2-}$ series are: chloride **1**, 614, 634, 667, 691; bromide **1a**, 645, 668, 698, 723; iodide **1b**, with values for $2[NEt_4]^+[CoI_4]^{2-}$ in parentheses, 698 (697), 727 (725), 757 (sh) [766 (sh)], 784 (781) nm. The values generally match those previously reported,[8,9] apart from some variation shown by the $[CoI_4]^{2-}$ ion in solution. The solid-state spectrum of the iodide $[Co(pyo)_6]^{2+}2I^-$ **2**, with octahedral co-ordination only, shows weak, poorly resolved bands at 508, 545 and 565 nm.

The reflectance spectrum from the mixed-ligand anion $[Co(pyo)I_3]^-$ in **5** shows a broad band with components at 650, 696, 710 and 768 nm. Through reduction in the formal charge, the averaged centre of the absorption lies at *ca.* 698 nm, as compared with 755 nm for $[CoI_4]^{2-}$.

Infrared Spectra.—In addition to the relevance to general relationships, the spectra of the Me_3NO derivatives at below 600 cm^{-1} (Table 3) serve to (*i*) confirm the structure of **4**, and (*ii*) provide evidence on metal–oxygen frequencies.

(*i*) The spectrum of compound **4** shows a single sharp Co–I stretching frequency at 204 cm^{-1}, but no identifiable bending frequency. This is consistent with there being *one* Co–I linkage. For comparison, **8** shows a Co–I absorption at 205 cm^{-1}, and one at 108 cm^{-1} which is probably a δ(Co–I) mode.

(*ii*) The question of M–O frequencies with this ligand seems to have received no attention since discussion in 1968.[13,17] There is the rather high-frequency band at 550–570 cm^{-1} and there are two weaker bands in the 250–300 cm^{-1} range. It can now be suggested that with the low M–O–N angles (116–126°) now found in the present ionic and molecular[12] complexes there is a strong coupling between ν(M–O) and a deformation

Table 3 Infrared spectra (cm^{-1})

	L = Me_3NO	ν(M–X)	ν(M–O)[a]	δ(M–O)	Ligand bands, 500–200 cm^{-1}[b]
3	$[CoL_4]^{2+}2I^-$	—	562s	292mw, 258mw	482s, 403m, 383m
4	$[CoL_3I]^+I^-$	204m	563s (br)	293mw, 258mw	483s, 404m, 382m
	$[CoL_2Cl_2]$	300s, 282s	564s	*c*	490 (sh), 476s, 410m, 385m
	$[CoL_2Br_2]$	227s	567s, 552 (sh)	310w, 262w	476s, 406m, 378mw
	$[CoL_2I_2]$	205s	572s	298vw, 260mw	479s, 405m, 378m
	$[ZnL_2Cl_2]$	304s, 276s	554s	*c*	482 (sh), 471s, 404m, 385m
	$[ZnL_2Br_2]$	214s, 189ms	556s	276ms, 256m	487 (sh), 473s, 400m, 276m
	$[ZnL_2I_2]$	185s	555s	272m, 251m	491s, 475s, 402m, 380m
	L = pyo				
2	$[CoL_6]^{2+}2I^-$	—	328ms		490s, 471s
1	$[CoL_6]^{2+}[CoCl_4]^{2-}$	290s	349m, 330m		489m, 464s
1a	$[CoL_6]^{2+}[CoBr_4]^{2-}$	229s	349m, 326mw		489s, 461s
1b	$[CoL_6]^{2+}[CoI_4]^{2-}$	200s	341s, 326 (sh)		491w, 463s, (162w)[d]
1c	$[ZnL_6]^{2+}[ZnBr_4]^{2-}$	205s	331s, 316s		494w, 463s, (150m)[d]
6	$[ZnL_6]^{2+}2[ZnLI_3]^-$	212m, 182s (br)	343ms, 324m		490m, 477ms, 460ms, (150 ms)[d]
5a	$[NEt_4]^+[ZnLI_3]^-$	212m, 190s, 174m	363s[e]		470 (sh), 450m (br), (138w)[d]
5	$[NEt_4]^+[CoLI_3]^-$	226m, 206m (sh), 199s	388m[e]		451w, (140w)[d]

[a] The ν(M–O) bands are characteristically less sharp than other bands. This is probably a consequence of the bond not being strongly directed. [b] Weak unassigned bands below 200 cm^{-1} are not listed. [c] The strong ν(M–Cl) bands carry only weak inflections arising from these modes. [d] Probably an (M–O) bending mode. [e] In anion.

Table 4 Minimum interligand approach distances (Å) in cations

	$[Co(Me_3NO)_4]^{2+}$	$[Co(pyo)_6]^{2+}$
C···O	3.133, 3.241, 3.225, 3.159[a]	3.360, 3.407
C···C(H···H)[b]	3.741 (2.43, 2.77)[c] 3.990 (2.65, 2.72)[c]	3.691 (2.68)

[a] The sequence gives the values for O(1) to O(4). [b] H···H corresponding to C···C, with H atoms in idealised positions. [c] These values are seen to be mostly higher than for $[Co(pyo)_6]^{2+}$.

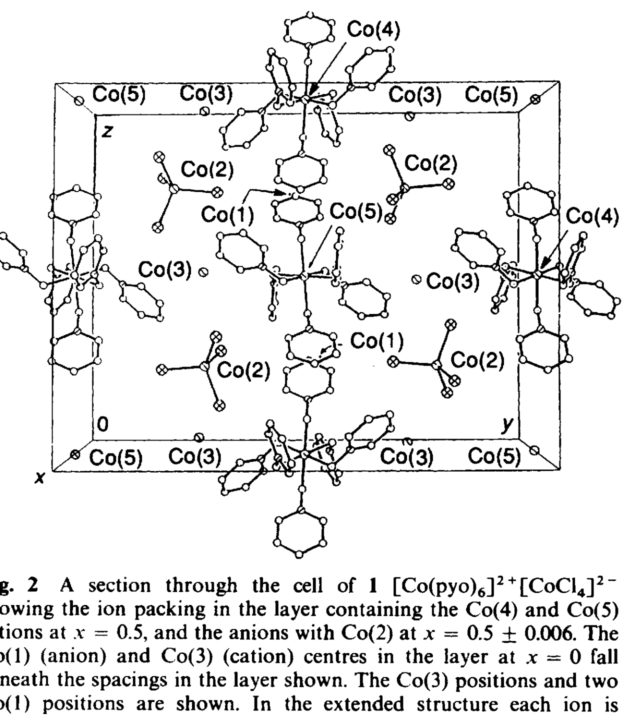


Fig. 2 A section through the cell of **1** $[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$ showing the ion packing in the layer containing the Co(4) and Co(5) cations at $x = 0.5$, and the anions with Co(2) at $x = 0.5 \pm 0.006$. The Co(1) (anion) and Co(3) (cation) centres in the layer at $x = 0$ fall beneath the spacings in the layer shown. The Co(3) positions and two Co(1) positions are shown. In the extended structure each ion is surrounded by eight of opposite charge

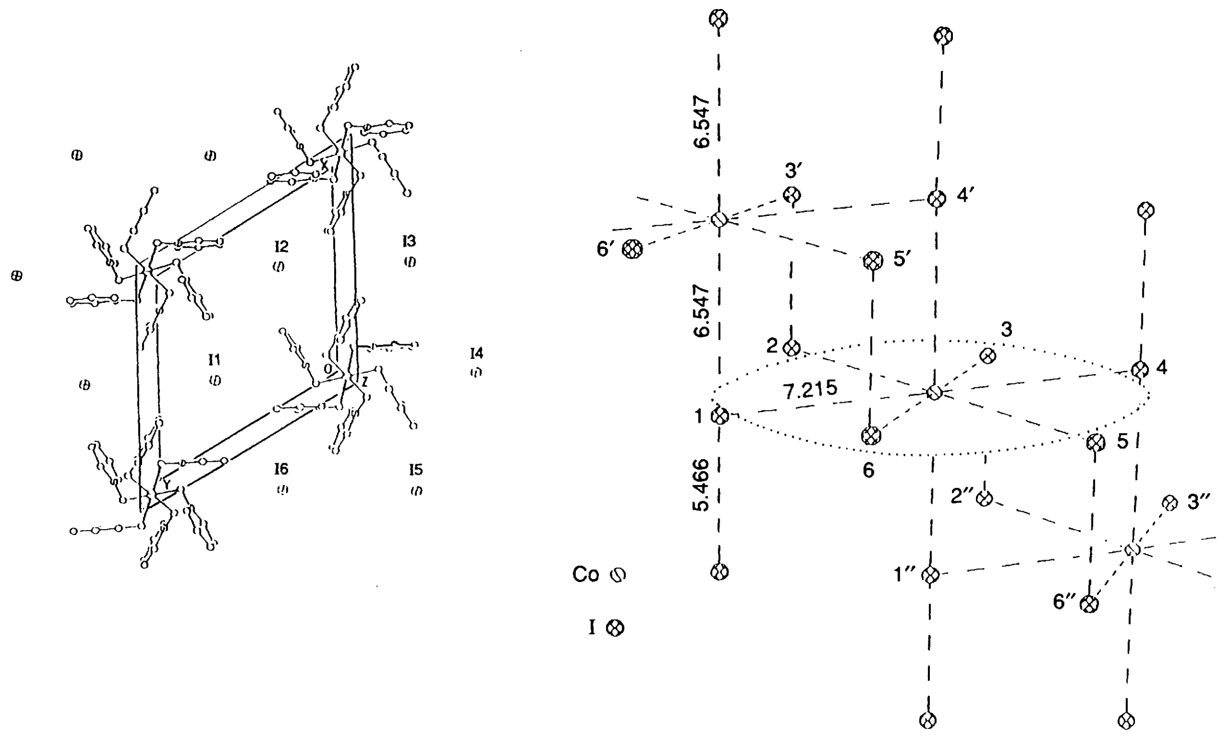
mode in the otherwise trigonally symmetrical ligand. The weaker bands lie in the expected range for a predominantly M–O bonding mode, but which is split through interactions with a degenerate deformation vibration of the ligand.[17–19]

Crystal Structures of Individual Compounds.—$[Co(pyo)_6]^{2+}$-$[CoCl_4]^{2-}$ **1**. The compound is confirmed to have this ionic constitution.[5] There are two crystallographically distinct anions centred on Co(1) and Co(2), and three sets of cations based on Co(3), Co(4) and Co(5) (Fig. 2). The unit cell includes four Co(3), two Co(4) and two Co(5) atoms. The Co(3) centres carry six independent ligands, but Co(4) and Co(5), which occupy special positions, each have a centrosymmetric ligand array. The ions, in checker-board type of arrangement, fall into layers parallel to {100}. The cobalt centres of successive layers are at, or close to, $x = 0$, 0.5, 1.0. Fig. 2 shows the $x = 0.5$ layer. It comprises the Co(2) anions and an alternation of the Co(4) and Co(5) cations. The Co(1) anions and the Co(3) cations of the $x = 0$ and 1 layers occupy the complementary checker-board positions covering the vacancies in the $x = 0.5$ layer. Each ion is thus surrounded by eight neighbours, affording an arrangement which, though distorted from cubic, can be related to the caesium chloride structure.

The cell parameters for the bromide **1a** show it to be isomorphous with the chloride, but faint additional spots in the axial photographs indicated disorder within the lattice. Cation disordering, or interchange, would seem a possibility. Isomorphism extending to the iodide $[Co(pyo)_6]^{2+}[CoI_4]^{2-}$ **1b** is shown by powder diffraction (Table 2) and to the zinc compound $[Zn(pyo)_6]^{2+}[ZnBr_4]^{2-}$ **1c** by matching cell parameters.

The highest frequency Co–X bands in the spectra of this $[Co(pyo)_6]^{2+}[CoX_4]^{2-}$ series lie at 290, 229 and 200 cm^{-1}, for X = Cl, Br and I respectively. Here, there should be minimum disturbance of anion vibrations by the large symmetrical cations, and the band splitting, hitherto observed,[20] does not occur.

$[Co(pyo)_6]^{2+}2I^-$ **2**. As with $[Co(pyo)_6]^{2+}2ClO_4^-$,[21] the cation has $R\bar{3}$ symmetry, with the CoO_6 co-ordination unit deviating only slightly from O_h. The geometry of the pyo ligand lends itself to this particular configuration, which produces no C···C or C···O approach distances below the sum of the relevant van der Waals radii (Table 4). Fig. 3 shows the cation–iodide distribution within the trigonal symmetry. It will be seen that two iodide ions of the cobalt environment occupy apical positions, 6.547 Å, along the trigonal axis. Six iodides lie at 7.224 Å, alternately 0.362 Å above and below the equatorial plane, with the whole set falling into a columnar arrangement. Each cation has eight surrounding iodide ions, and each iodide is surrounded by four cations, with the remaining apical position of its otherwise trigonal-bipyramidal environment occupied by another iodide 5.466 Å distant. The displacement of this



(a) (b)

Fig. 3 (*a*) The development of the trigonal packing of the ions $[Co(pyo)_6]^{2+}$ and I^-, as seen down the *z* axis. (*b*) A view oblique to the iodide ring, I(1)–I(6), showing the columnar arrangement of the ions and the ion environments. The spacings are indicated with 7.215 Å being the distance to the dotted edge of the equatorial plane. The up-and-down crinkling of the iodide ring is slightly exaggerated. Distances in Å

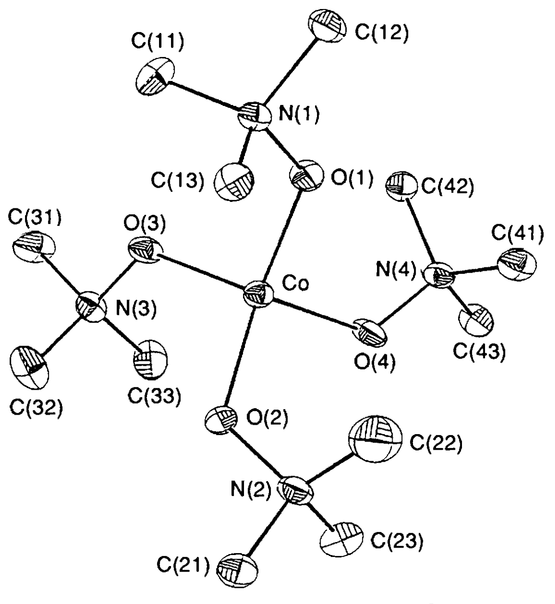


Fig. 4 The distorted tetrahedral $[Co(Me_3NO)_4]^{2+}$ cation as seen almost along the bisectors of the angles O(1)–Co–O(2) (126.4°) and O(3)–Co–O(4) (120.3°). The closest $CH_3 \cdots O$ approaches are C(42) ··· O(1), C(32) ··· O(2), C(11) ··· O(3) and C(23) ··· O(4)

neighbouring iodide pair *towards* each other in relation to the equatorial planes is noteworthy. The *c* dimension of the cell, 18.561 Å, arises from the (2 × 6.547) + 5.466 Å addition.

$[Co(Me_3NO)_4]^{2+}2I^-$ **3**. The cation geometry provides geometrical evidence for the restriction of the co-ordination number to four, through the spread of the methyl groups (see Fig. 4). It becomes evident from approach distances that the steric constraint is imposed by interligand $CH_3 \cdots O$ approaches, rather than $CH_3 \cdots CH_3$. Even with four-co-ordination there are already $CH_3 \cdots O$ distances of 3.2 Å or less (Table 4), as compared with a van der Waals sum 3.2–3.4 Å. For comparison the $[Co(pyo)_6]^{2+}$ cation of **2** gives 3.36 Å as the shortest C ·· O distance, and this with a Co–O–N angle of only 118.7° as against 124.6° (average) in $[Co(Me_3NO)_4]^{2+}$. It can be suggested that the need to equalise $CH_3 \cdots O$ approaches at as high a value as possible underlies the marked distortion (flattening) of the CoO_4 tetrahedron, with its O(1)–Co–O(2) and O(3)–Co–O(4) angles splayed to 126.4 and 120.3° respectively. The four ligands show varying O′–Co–O–N and Co–O–N–C torsion angles.

Within the cell, minimum intercation C ··· C distances have the usual values of 3.6–3.75 Å and the minimum C ··· I are 3.8–4.0 Å. The iodide ions are enclosed irregularly, with I(1) having three cation (methyl) approaches below 4.0 Å, and I(2) five such distances.

$[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$ **6**. The cation is centrosymmetric, with Zn(1) at the inversion centre of the $P\bar{1}$ cell. The anions Zn(2i) and Zn(2′ii) are in this centrosymmetric relationship. As seen along the *x* axis (Fig. 5), the anions and cations lie in alternate bands. The anion bands are 'doubled' through pairing of two layers containing respectively the anions centred on Zn(2) and Zn(2′). This provides interanion neutralisation of the anion polarity through I(2) and I(3) approaches to the pyo rings of partner anions. The Zn, I(2), I(3) plane is almost parallel to the ring planes (interplane angle 5.4°). Only I(1) atoms are directed specifically towards the cations. Neutralisation of cation charge is thus effected by the residual field from the doubled anion band.

Experimental

Preparation of Compounds.—As a general procedure the compounds were obtained by direct reaction of a metal halide with an excess of ligand in boiling ethanol with sufficient triethoxymethane to maintain anhydrous conditions. Reactant ratios were varied to avoid overlooking other possible products. Crystals for diffraction were from dilute mother-liquors. The

Table 5 Crystal data, experimental conditions, and refinement

	1 $[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$	**2** $[Co(pyo)_6]^{2+}2I^-$	**3** $[Co(Me_3NO)_4]^{2+}2I^-$	**6** $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$
M	830.25	883.4	613.1	1718.3
Crystal size/mm	0.39 × 0.41 × 0.16	0.20 × 0.16 × 0.15	0.24 × 0.22 × 0.21	0.15 × 0.30 × 0.70
Crystal system	Monoclinic	Trigonal	Monoclinic	Triclinic
Space group (Z)	$P2_1/c$(8)	$R\bar{3}$(3)	$P2_1/n$(4)	$P\bar{1}$(1)
a/Å	14.705(3)	12.497(2)	10.597(4)	9.227(3)
b/Å	24.253(4)	12.497(2)	12.448(3)	9.557(3)
c/Å	18.869(4)	18.561(3)	17.900(4)	16.102(2)
α/°	90	90	90	73.27(2)
β/°	91.27(2)	90	95.14(3)	74.83(2)
γ/°	90	120	90	89.43(2)
U/Å^3	6727.8(2.5)	2510.4(1.1)	2351.7(1.2)	1308.8(6)
$D_c(D_m)$[a]	1.64(1.58)	1.75(1.72)	1.73(1.70)	2.18(2.11)
F(000)	3376	1299	1204	808
μ(Mo-Kα)/cm^{-1}	13.56	23.85	33.45	49.53
h, k, l ranges	0–23, 0–29, −18 to 18	0–15, 0–15, −23 to 23	0–13, 0–15, −22 to 22	0–9, −10 to 10, −16 to 16
Unique reflections	10 075	982	4140	5147
Reflections used [$I > 3\sigma(I)$]	5736	834	3242	4578
Transmission range	0.761–0.608	0.717–0.619	0.699–0.561	0.861–0.711
Parameters refined	868	89	245	292
Weighting g	0.0002	0.000 33	0.000 08	0.000 61
Residual density, e Å^{-3}	0.45, −0.44	0.32, −0.51	0.38, −0.60	1.19, −2.66
$R(R')$[b]	0.0421 (0.0408)	0.0237 (0.0283)	0.0246 (0.0264)	0.0311 (0.0462)

[a] Density measured at room temperature. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$; $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

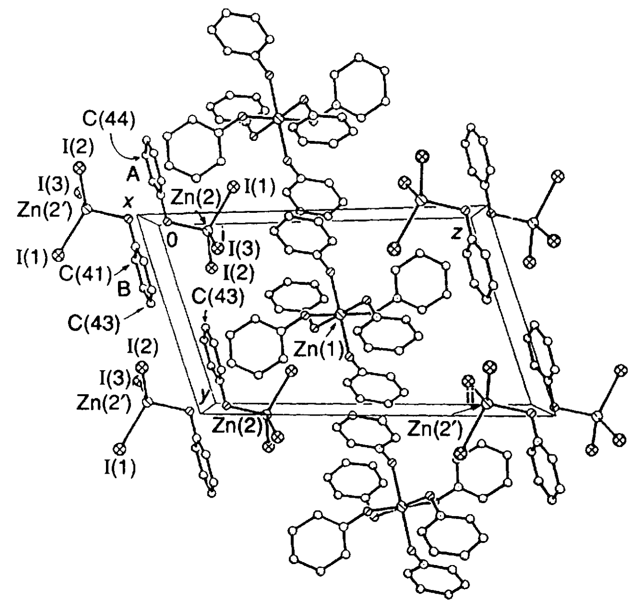


Fig. 5 The ion packing within the triclinic cell of $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$ **6**. The anion packing into composite double layers, containing Zn(2) and Zn(2'), to provide C ··· I interanion approaches is apparent. Atom I(2) also approaches C(43) in the same layer. Symmetry codes are: Zn(1) and Zn(2i) at x,y,z; Zn(2'ii) at $1 - x$, $1 - y$, $1 - z$

crystals were rinsed with triethoxymethane and diethyl ether, and dried under nitrogen.

$[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$ **1**. Cobalt(II) chloride (2.5 mmol) and pyo (7.5 mmol) in ethanol (12 cm^3) with $CH(OEt)_3$ (1.5 cm^3), stirred for 5 min, gave compound **1** as a bright green powder[10] [Found (Calc.): C, 43.4 (43.4); H, 3.5 (3.6); N, 10.3 (10.1)%]. The yellow-green bromide $[Co(pyo)_6]^{2+}[CoBr_4]^{2-}$ **1a** was obtained similarly [Found (Calc.): C, 35.7 (35.7); H, 2.8 (2.9); N, 8.4 (8.3)%].

Using cobalt(II) iodide and pyo in a 1:3 molar ratio, $[Co(pyo)_6]^{2+}[CoI_4]^{2-}$ **1b** separated as a buff powder [Found (Calc.): C, 29.4 (30.1); H, 2.2 (2.5); N, 6.6 (7.0)%]. Extraction with boiling ethanol slowly brought this tetraiodo complex into solution, though only with decomposition to free cobalt iodide and to compound **2**, which crystallised on cooling.

$[Co(pyo)_6]^{2+}2I^-$ **2**. Cobalt(II) iodide tetrahydrate (0.5 mmol) and pyo (6 mmol) in ethanol (8 cm^3)–triethoxymethane (2 cm^3) were stirred for 20 min. The solution was filtered from the buff precipitate and produced orange-pink crystals of compound **2** on cooling [Found (Calc.): C, 40.4 (40.8); H, 3.2 (3.4); N, 9.5 (9.5)%].

$[Co(Me_3NO)_4]^{2+}2I^-$ **3** *and* $[Co(Me_3NO)_3I]^+I^-$ **4**. The first compound was obtained using cobalt(II) iodide tetrahydrate (1 mmol) and Me_3NO (5 mmol) in ethanol (6 cm^3). The purple product was recrystallised from nitromethane. The use of cobalt iodide and Me_3NO in 1:3 molar ratio gave fine blue-violet needles of compound **4** as a distinct crystalline phase. It gave d values (with relative intensities) of 6.463 (42), 5.823 (26), 5.422 (30), 5.052 (43), 4.091 (46), 3.665 (35), 3.165 (100) and 2.024 (55). Attempted recrystallisation from ethanol and other solvents gave, as decomposition products, violet crystals of **3** with the deep blue molecular species **8** remaining in solution.

$[Co(Me_3NO)_4]^{2+}2Br^-$ **3a**. This bromide, isomorphous with the iodide **3**, crystallised when using a 1:10 molar ratio of cobalt:ligand. The crystals are highly hygroscopic. The cell parameters match those of **3**: $a = 10.511(4)$, $b = 11.918(4)$, $c = 17.638(7)$ Å, $\beta = 94.75(3)°$, and $U = 2202.0(1.5)$ Å^3. A structure refinement gave convergence at $R(R') = 0.0327$ (0.0367).

$[NEt_4]^+[Co(pyo)I_3]^-$ **5**. Cobalt(II) iodide tetrahydrate, pyo, and tetraethylammonium iodide (1 mmol of each) were dissolved in ethanol (12 cm^3)–triethoxymethane (2 cm^3), and the solution concentrated to half volume. Dark green crystals of compound **5** separated on cooling. The mother-liquor was poured off because continuing crystallisation gave yellow-green plates of $2[NEt_4]^+[CoI_4]^{2-}$ [Found (Calc.) for **5**: C, 23.5 (23.5); H, 4.05 (3.80); N, 4.1 (4.2)%].

$[NEt_4]^+[Zn(pyo)I_3]^-$ **5a**. Zinc iodide, tetraethylammonium iodide and pyo (1 mmol of each) were stirred in boiling ethanol (12 cm^3)–triethoxymethane (1.5 cm^3) for 50 min. Free tetra-

Table 6 Bond lengths (Å) and angles (°)

1 $[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$

Co(1)–Cl	2.293(2), 2.283(2), 2.275(2), 2.283(2)
Co(2)–Cl	2.283(2), 2.284(2), 2.281(2), 2.282(2)
Co(3)–O	2.057(3), 2.086(4), 2.073(4), 2.090(4), 2.084(4), 2.095(4)
Co(4)–O	2.083(4), 2.101(4), 2.058(4)
Co(5)–O	2.080(4), 2.120(3), 2.055(4)
N–O (av.)	1.335(6), 1.339(6), 1.337(6) [on Co(3), Co(4), Co(5) centres]
Cl–Co–Cl	106.7–110.5
O–Co–O	85.8–95.7
Co–O–N	116.1–120.3; 118.1(2) (av.)

2 $[Co(pyo)_6]^{2+}2I^-$

Co–O	2.086(2)
N–O	1.342(4)
Co–O–N	118.7(2)

3 $[Co(Me_3NO)_4]^{2+}2I^-$

Co–O	1.948(3), 1.954(3), 1.941(3), 1.950(3)
N–O	1.411(4), 1.420(5), 1.417(4), 1.403(4)
Co–O–N	125.4(2), 122.4(2), 124.0(2), 126.4(2)
O–Co–O	126.4(1), 120.3(1), 102.7(1), 106.2(1), 101.8(1), 101.1(1)
C···O	3.136, 3.238, 3.223, 3.151

6 $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$

Zn(1)–O	(cation) 2.151(4), 2.099(4), 2.046(4)
Zn(2)–O	(anion) 2.019(4)
Zn(2)–I	2.576(3), 2.602(3), 2.606(3)
N–O	(cation) 1.336(5) (av.); (anion) 1.342(6)
O–Zn(1)–O	87.4–90.5
I–Zn(2)–I	112.0(1), 113.7(1), 115.5(1)
O–Zn(2)–I	106.3(1), 101.7(1), 106.3(1)
Zn–O–N	(cation) 122.3(2) (av.); (anion) 116.8(2)

Table 7 Atomic coordinates (× 10^4) for $[Co(pyo)_6]^{2+}[CoCl_4]^{2-}$ **1**

Atom	*x*	*y*	*z*
Co(1)	173(1)	374(1)	2532(1)
Cl(11)	617(1)	−529(1)	2446(1)
Cl(12)	497(1)	697(1)	3645(1)
Cl(13)	−1359(1)	443(1)	2365(1)
Cl(14)	911(1)	890(1)	1711(1)
Co(2)	4940(1)	7156(1)	7501(1)
Cl(21)	5021(1)	8093(1)	7602(1)
Cl(22)	6316(1)	6845(1)	7129(1)
Cl(23)	3897(1)	6878(1)	6663(1)
Cl(24)	4586(1)	6829(1)	8595(1)
Co(3)	55(1)	−2379(1)	4882(1)
O(1)	445(2)	−2476(1)	5928(2)
N(1)	−189(3)	−2590(2)	6405(2)
C(11)	−241(4)	−3108(2)	6661(3)
C(12)	−861(4)	−3237(3)	7166(3)
C(13)	−1434(4)	−2832(3)	7412(3)
C(14)	−1377(4)	−2309(2)	7141(3)
C(15)	−750(4)	−2188(2)	6633(3)
O(2)	1123(3)	−2899(1)	4611(2)
N(2)	1233(3)	−3364(2)	4979(2)
C(21)	1824(4)	−3385(2)	5543(3)
C(22)	1943(4)	−3859(2)	5917(3)
C(23)	1466(4)	−4331(3)	5731(3)
C(24)	872(4)	−4301(2)	5152(4)
C(25)	760(4)	−3815(2)	4775(3)
O(3)	−225(2)	−2264(2)	3810(2)
N(3)	471(3)	−2341(2)	3374(2)
C(31)	1026(4)	−1918(2)	3226(3)
C(32)	1738(4)	−1999(3)	2771(3)
C(33)	1869(4)	−2510(2)	2456(3)
C(34)	1275(4)	−2935(2)	2617(3)
C(35)	584(4)	−2844(2)	3083(3)
O(4)	954(2)	−1716(1)	4809(2)
N(4)	1692(3)	−1717(2)	5236(2)
C(41)	2459(4)	−1970(2)	5024(3)
C(42)	3226(4)	−1969(2)	5457(4)
C(43)	3216(4)	−1699(2)	6103(3)
C(44)	2428(4)	−1427(2)	6293(3)
C(45)	1665(4)	−1449(2)	5862(3)
O(5)	−1077(2)	−1891(1)	5081(2)
N(5)	−1362(3)	−1533(2)	4591(2)
C(51)	−2216(4)	−1573(2)	4314(3)
C(52)	−2525(4)	−1223(2)	3797(3)
C(53)	−1948(4)	−812(2)	3547(3)
C(54)	−1074(4)	−768(2)	3846(3)
C(55)	−795(4)	−1129(2)	4372(3)
O(6)	−825(3)	−3051(1)	5004(2)
N(6)	−1695(3)	−3011(2)	4800(2)
C(61)	−1920(4)	−2987(2)	4102(3)
C(62)	−2825(4)	−2961(2)	3885(3)
C(63)	−3499(4)	−2967(2)	4387(3)
C(64)	−3253(4)	−2990(2)	5091(4)
C(65)	−2353(4)	−3005(2)	5297(3)
Co(4)	5000	0	5000
O(7)	5938(3)	609(1)	4748(2)
N(7)	6761(3)	566(2)	5063(2)
C(71)	6884(4)	762(2)	5724(3)
C(72)	7716(5)	716(3)	6058(3)
C(73)	8421(5)	469(3)	5717(4)
C(74)	8291(4)	277(3)	5037(4)
C(75)	7446(4)	326(2)	4706(3)
O(8)	4000(3)	582(1)	5254(2)
N(8)	3812(3)	970(2)	4768(2)
C(81)	3066(4)	922(2)	4352(3)
C(82)	2843(4)	1324(2)	3868(3)
C(83)	3409(4)	1776(2)	3787(3)
C(84)	4178(4)	1815(2)	4213(3)
C(85)	4367(4)	1411(2)	4712(3)
O(9)	4494(2)	51(2)	3977(2)
N(9)	5106(3)	70(2)	3465(2)
C(91)	5375(4)	557(2)	3218(3)
C(92)	6013(4)	582(2)	2691(3)
C(93)	6357(4)	102(2)	2416(3)
C(94)	6058(4)	−398(2)	2680(3)
C(95)	5438(4)	−410(2)	3205(3)
Co(5)	5000	0	0
O(7″)	6176(3)	459(2)	−146(2)
N(7″)	6356(3)	889(2)	275(2)
C(71″)	7022(4)	848(2)	773(3)
C(72″)	7232(4)	1285(3)	1200(3)
C(73″)	6759(4)	1776(3)	1136(3)
C(74″)	6068(4)	1807(2)	609(4)
C(75″)	5886(4)	1362(2)	183(3)
O(8″)	4146(2)	702(1)	58(2)
N(8″)	3307(3)	684(2)	−226(3)
C(81″)	2585(4)	643(2)	197(3)
C(82″)	1720(4)	652(2)	−82(3)
C(83″)	1574(4)	686(2)	−807(3)
C(84″)	2326(4)	731(2)	−1233(3)
C(85″)	3191(4)	734(2)	−937(3)
O(9″)	5202(3)	72(2)	1077(2)
N(9″)	4474(3)	116(2)	1485(2)
C(91″)	4049(4)	−341(3)	1718(3)
C(92″)	3326(4)	−297(3)	2163(3)
C(93″)	3018(4)	215(3)	2357(3)
C(94″)	3460(4)	674(3)	2117(3)
C(95″)	4181(4)	621(2)	1682(3)

Table 8 Atomic coordinates (× 10^4) for $[Co(pyo)_6]^{2+}2I^-$ **2**

Atom	*x*	*y*	*z*
I	0	0	1472(1)
Co	0	0	5000
O	1531(2)	1075(2)	5650(1)
N	2024(2)	515(2)	6031(1)
C(1)	2650(3)	48(4)	5697(2)
C(2)	3161(3)	−527(4)	6087(2)
C(3)	3026(3)	−623(4)	6829(2)
C(4)	2381(3)	−127(3)	7161(2)
C(5)	1882(3)	440(3)	6754(2)

Table 9 Atomic coordinates (× 10^4) for $[Co(Me_3NO)_4]^{2+}2I^-$ **3**

Atom	*x*	*y*	*z*
I(1)	2242(1)	1443(1)	839(1)
I(2)	7006(1)	4881(1)	2219(1)
Co	2289(1)	2151(1)	4192(1)
O(1)	1612(3)	3315(2)	4765(2)
O(2)	4062(3)	1938(2)	4009(2)
O(3)	1792(3)	882(2)	4722(2)
O(4)	1532(3)	2454(2)	3181(2)
N(1)	2000(3)	3567(3)	5519(2)
C(11)	1687(5)	2666(4)	6020(2)
C(12)	1272(4)	4550(4)	5703(3)
C(13)	3373(4)	3809(4)	5598(2)
N(2)	4693(3)	2608(3)	3520(2)
C(21)	6079(4)	2439(4)	3702(3)
C(22)	4395(5)	3758(3)	3645(3)
C(23)	4332(4)	2282(4)	2731(2)
N(3)	2100(3)	−182(3)	4523(2)
C(31)	1327(5)	−913(4)	4949(3)
C(32)	3465(4)	−364(4)	4742(3)
C(33)	1804(5)	−340(4)	3703(3)
N(4)	411(3)	3030(3)	2990(2)
C(41)	730(4)	4200(3)	3010(3)
C(42)	−566(4)	2790(4)	3515(2)
C(43)	−60(4)	2705(4)	2218(2)

Table 10 Atomic coordinates (× 10^4) for $[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$ **6**

Atom	*x*	*y*	*z*
Zn(1)	5 000	5 000	5 000
O(1)	2 983(4)	4 961(3)	6 046(2)
N(1)	2 748(4)	4 169(4)	6 908(2)
C(11)	2 198(5)	4 812(5)	7 549(3)
C(12)	1 890(6)	3 997(6)	8 454(3)
C(13)	2 150(5)	2 531(6)	8 693(3)
C(14)	2 709(6)	1 898(5)	8 015(3)
C(15)	3 020(5)	2 729(5)	7 112(3)
O(2)	4 527(3)	2 791(3)	5 129(2)
N(2)	5 646(4)	1 963(4)	4 887(2)
C(21)	6 465(5)	1 354(5)	5 459(3)
C(22)	7 568(6)	422(5)	5 228(4)
C(23)	7 815(6)	147(6)	4 409(4)
C(24)	6 978(6)	805(5)	3 824(4)
C(25)	5 882(5)	1 710(5)	4 082(3)
O(3)	6 197(4)	4 281(3)	5 929(2)
N(3)	7 196(4)	5 160(4)	6 040(2)
C(31)	8 377(5)	5 839(6)	5 346(3)
C(32)	9 447(6)	6 661(6)	5 494(3)
C(33)	9 327(6)	6 811(5)	6 333(4)
C(34)	8 072(6)	6 122(5)	7 036(3)
C(35)	7 042(5)	5 307(5)	6 863(3)
I(1)	11 011(1)	−1 903(1)	12 872(1)
I(2)	10 234(1)	2 374(1)	11 325(1)
I(3)	14 639(1)	1 512(1)	11 881(1)
Zn(2)	12 218(1)	484(1)	11 648(1)
O(4)	12 867(4)	−25(3)	10 478(2)
N(4)	13 058(4)	−1 445(4)	10 538(2)
C(41)	14 275(5)	−2 062(5)	10 754(3)
C(42)	14 469(5)	−3 521(5)	10 799(3)
C(43)	13 419(6)	−4 340(5)	10 646(3)
C(44)	12 185(5)	−3 655(5)	10 400(3)
C(45)	12 020(5)	−2 209(5)	10 353(3)

ethylammonium iodide crystallised first, followed by clear needles of the zinc complex [Found (Calc.): C, 23.4 (23.25); H, 3.9 (3.8); N, 4.15 (4.2)%]. Isomorphism of **5a** with **5** was shown by powder diffraction. There was correspondence of the infrared spectra of **5**, **5a** and **6** in the ν(M–I) region (Table 3).

$[Zn(pyo)_6]^{2+}2[Zn(pyo)I_3]^-$ **6**. *Zinc iodide* (1 mmol) and pyo (5 mmol) in ethanol (6 cm^3)–triethoxymethane (2 cm^3) were used. Acicular crystals of the compound $[Zn(pyo)_2I_2]$[22,23] separated on cooling, presumably through preferential nucleation, but after 24 h they had given place to 'cubes' and prisms of **6** [Found (Calc.) for the needles: C, 23.7 (23.6); H, 1.7 (2.0); N, 5.6 (5.5). For **6**: C, 28.0 (28.1); H, 2.45 (2.35); N, 6.4 (6.5)%].

It was not found possible to obtain $[Zn(pyo)_6]^{2+}[ZnI_4]^{2-}$, but analytically pure samples of $[Zn(pyo)_6]^{2+}[ZnBr_4]^{2-}$ **1c** and $[Zn(Me_3NO)_4]^{2+2}I^-$ **7** were crystallised.

Spectra.—Spectrometers used were: Perkin-Elmer UV/VIS Lambda 2; and for infrared, Philips Analytical SP3-300 (to 240 cm^{-1}, with mylar film calibration) and Digilab FTS-60(500–60 cm^{-1}). The strong ν(M–X) and ν(M–O) bands were identified as additional to ligand bands and were checked through intercomparisons. Bending modes in these compounds are generally weak and assignments are offered only where bands appear conspicuously at frequencies which are self-consistent for related compounds.

X-Ray Structure Analysis.—The determinations followed our usual procedure,[24] using a Nicolet R3M four-circle diffractometer, with the crystal at 150–170 K and ω scanning. Reflections were collected over the 2θ range 4–50 or 60°. Details for individual compounds are given in Table 5. Heavy atoms were located from Patterson maps and other atoms from Fourier difference synthesis. Refinements were made with anisotropic thermal parameters; function minimised $\Sigma w(|F_o| - |F_c|)^2$ with reflection weights $w = [\sigma^2|F_o| + gF_o{}^2]^{-1}$. Hydrogen atoms were introduced at idealised positions, and for compound **2** their positions were 'refined'. The SHELXTL PC package[25] was used for data reduction and structure solution.

Bond lengths and angles around co-ordination centres are given in Table 6, atomic coordinates in Tables 7–10.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are much indebted to Dr. Ward Robinson who provided the opportunity for the crystallographic work. We are indebted also to Dr. James McQuillan for assistance with running infrared spectra at the University of Otago. One of us (S. J.) participated during leave from the Changchun Institute for Applied Chemistry, Changchun, China.

References

1 D. W. Meek, D. K. Straub and R. S. Drago, *J. Am. Chem. Soc.*, 1960, **82**, 6013.

2 R. L. Carlin, *J. Am. Chem. Soc.*, 1961, **83**, 3773.

3 D. W. Herlocker and R. S. Drago, *Inorg. Chem.*, 1968, **7**, 1479.

4 P. L. Goggin, *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, p. 497.

5 J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, 1964, **3**, 775.

6 K. Issleib and A. Kreibich, *Z. Anorg. Allg. Chem.*, 1961, **313**, 338.

7 W. Saak and S. Pohl, *Z. Anorg. Allg. Chem.*, 1987, **552**, 186.

8 N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.

9 F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, 1961, **83**, 4690.

10 J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, 1961, **83**, 3770.

11 D. W. Herlocker, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2197.

12 S. Jin, M. Nieuwenhuyzen, W. T. Robinson and C. J. Wilkins, *Acta Crystallogr., Sect. C*, 1992, **48**, 274.

13 S. H. Hunter, V. M. Langford, G. A. Rodley and C. J. Wilkins, *J. Chem. Soc. A*, 1968, 305.

14 N. M. McConnell, R. O. Day and J. S. Wood, *Acta Crystallogr., Sect. C*, 1986, **42**, 1094.

15 H. C. A. King, E. Körös and S. M. Nelson, *J. Chem. Soc.*, 1963, 5449.

16 E. P. Linton, *J. Am. Chem. Soc.*, 1940, **62**, 1945.

17 M. Kimura, Y. Kuroda and I. Shibuya, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2026.

18 P. A. Giguère and D. Chin, *Can. J. Chem.*, 1961, **39**, 1214.

19 S. Kida, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 712.

20 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1977, p. 137.

21 J. S. Wood, R. K. Brown and M. S. Lehmann, *Acta Crystallogr., Sect. C*, 1986, **42**, 410.

22 G. Schmauss and H. Specker, *Z. Anorg. Allg. Chem.*, 1968, **363**, 113.

23 G. Sawitzki and H.-G. von Schnering, *Chem. Ber.*, 1974, **107**, 3266.

24 W. T. Robinson, C. J. Wilkins and Z. Zhang, *J. Chem. Soc., Dalton Trans.*, 1988, 2187.

25 G. M. Sheldrick, SHELXTL PC, An Integrated System for Data Collection, Processing, and Structure Solution and Refinement, Siemens Analytical X-ray Instruments, Madison, WI, 1990.

Received 15*th November* 1991; *Paper* 1/05804E