1006. *Metal Complexes of Picolinic Acid* N-*Oxide.*

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The behaviour of picolinic acid *N*-oxide towards transition and non-transition metal ions has been investigated. Complexes of Ca, Mg, Cr(III), Mn(II), Mn(III), Fe(II), Fe(III), Co(II), Co(III), Ni(II), Cu(II), and Zn(II) have been characterised, and their magnetic properties and ultraviolet, visible, and infrared absorption spectra have been studied. Infrared frequencies have been assigned to the carboxyl and amine oxide groups. On the basis of this infrared study the complexes have been classified in two groups, differing in bond type and structure. The visible absorption spectra have been assigned as far as possible, and the crystal-field strength of the ligand is shown to be comparable with the field of two water molecules.

DURING the past decade there has been much investigation of the donor properties of Group VB elements towards transition metals, and many ligands utilising nitrogen, phosphorus, arsenic, and antimony have been studied. More recently there has been interest in the oxidised forms of these ligands, particularly the phosphine[1] and arsine oxides.[2] Until last year, however, little had been published about the chemistry of the amine oxide ligands. In 1961 a number of workers[3-6] published their results on the complex-forming ability of pyridine 1-oxide, and Heller[7] published a short communication on picolinic acid *N*-oxide.

We had been working independently on picolinic acid *N*-oxide (referred to below as " the ligand " or, in formulæ, as PicO) and here we describe its behaviour with metals, especially those of the first transition series. We have briefly reported[8] some details of this work. Complexes of the bivalent ions Mn, Fe, Co, Ni, Cu, Zn, Mg, and Ca and of the tervalent ions Cr, Mn, Fe, and Co are described. Hitherto[7] only copper, zirconium, beryllium, and uranium derivatives had been characterised. The infrared spectra of the complexes have been studied, with special regard to absorptions arising from the carboxyl and the amine oxide groups. With this study we have been able in some cases to determine the type of bonding present. Ultraviolet and visible absorption spectra are reported and the absorption bands are assigned as far as possible. In some cases we have been able to calculate values for the crystal-field parameter Dq and the Racah parameter B. With one exception all the complexes are shown by their magnetic properties to be spin-free.

Infrared Spectra.—A study of the infrared spectra of these amine oxide–metal complexes suggests that the frequencies pertaining to the carboxyl- and amine-oxygen atoms can be correlated with the geometric structure of the complexes and with the degree of covalency in the metal–oxygen bond. Katritzky and Hands[9] have already dealt with the infrared spectra of the 2-substituted pyridine oxides, and on the basis of their assignments we distinguish the carboxyl and amine oxide stretching frequencies from other vibrations. The results are listed in Table 1.

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[1] Issleib, Tzschach, and Frohlich, *Z. anorg. Chem.*, 1959, **298**, 164; Issleib and Mitscherling, *ibid.*, 1960, **304**, 73; Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1960, **82**, 5771; Cotton *et al.*, *J.*, 1960, 1873, 1878, 1959, 2265.

[2] Goodgame and Cotton, *J. Amer. Chem. Soc.*, 1960, **82**, 5774; Phillips and Tyree, *ibid.*, 1961, **83**, 1806; Goodgame, Goodgame, and Cotton, *ibid.*, p. 4161.

[3] Quagliano, Fujita, Franz, Phillips, Walmsley, and Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 3770; Nyholm and Turco, *J.*, 1962, 1121.

[4] Carlin, *J. Amer. Chem. Soc.*, 1961, **83**, 3775; Carlin, Roitman, Dankleff, and Edwards, *Inorg. Chem.*, 1962, **1**, 182.

[5] Garcia and Orchin, *J.*, 1961, 2254; Hieber and Lipp, *Chem. Ber.*, 1959, **92**, 2085.

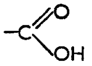
[6] Issleib and Kreibich, *Z. anorg. Chem.*, 1962, **313**, 338; Heller, *Bull. Res. Council Israel*, 1960, **9**, *A*, 245; Harris, Kokot, Lenzer, and Lockyer, *Chem. and Ind.*, 1962, 651.

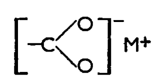
[7] Heller, *Bull. Res. Council Israel*, 1961, **10**, *A*, 7.

[8] Lever, Lewis, and Nyholm, Proc. 7th Internat. Conference on Co-ordination Chemistry, 1962 Abs., p. 49.

[9] Katritzky and Hands, *J.*, 1958, 2195.

In the region 1658—1590 cm.$^{-1}$, two strong bands are observed, within the ranges 1658—1618 and 1612—1590 cm.$^{-1}$. According to Katritzky and Hands[9] the νCC–νCN A_1 vibration, with electron-withdrawing substituents in the 2-position, lies in the range 1610—1594 cm.$^{-1}$. We conclude, therefore, that the lower of the two absorptions which we observe is the νCC–νCN A_1 vibration and that the higher vibration lying well outside this range is attributable to the carboxyl group (ν_1 in Table 1). Bands observed in the region 1500—1300 cm.$^{-1}$ agree well with Katritzky and Hands's data. There is, however, an additional band readily attributable to the carboxyl group (ν_2 in Table 1). Two bands assigned[9] to the $N^+–O^-$ stretching vibration are also listed (ν_3 and ν_4). In general, a carboxylic acid (Ia) exhibits[10] a ketone stretching frequency above 1700 cm.$^{-1}$ and a C–O single-bond frequency just below 1300 cm.$^{-1}$. When the carboxylate ion (Ib) is present, these two absorptions are replaced by the asymmetric and the symmetric stretching vibrations in the regions 1610—1550 and 1420—1300 cm.$^{-1}$, respectively. A large number of organic salts have been studied by Lecomte and his co-workers,[11] and all seem to fit this general scheme. When the metal forms a covalent bond to the carboxyl-oxygen (Ic), the band assigned as the asymmetric frequency in the free ion increases as the vibration takes on more ketonic character. Recent work by Nakomoto *et al.*[12,13] and by Sievers and Bailar[14] indicates that the limits for the " asymmetric " frequency with covalent


(Ia)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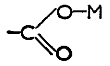
(Ic)

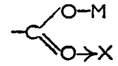
(Id: X = M) (Ie: X = H_2O)

TABLE 1.

Infrared, conductivity, and magnetic data.

	$\mu_{\text{eff.}}$ at 25° (B.M.)	κ‡	Infrared frequencies (cm.$^{-1}$)				
				ν_1	ν_2	ν_3	ν_4
PicOH ………………			1733, 1689	1626	1393	1290	1259
Ca((PicO)$_2$……………	0	—		1634	1376	1280	1238
Mg(PicO)$_2$,2H_2O ……	0	—	1689sh	1634	1387	1277	1232
Mn(PicO)$_2$,2H_2O ……	5·98	29	1695sh	1626	1383	1282	—
Fe(PicO)$_2$,2H_2O ……	5·36			1615	1379	1276	1229
Co(PicO)$_2$,2H_2O ……	4·90	10		1623	1385	1277	1230
Ni(PicO)$_2$,2H_2O ……	3·23	—		1616	1389	1272	1232
Cu(PicO)$_2$,2H_2O ……	1·88	—	1661sh	1634	1380	1282	1238
Zn(PicO)$_2$,1½H_2O ……	0		1689sh	1618	1381	1276	—
Cu(PicO)$_2$ ……………	1·87	—	1672	1650	1344	1259	1230
Be(PicO)$_2$*……………	0	—		1658	1335	1261	1247
Cr(PicO)$_3$,H_2O ………	3·77		1707	1647	1336	1279 † 1267	1241, 1232
Mn(PicO)$_3$……………	5·00	29		1639	1330	1276sh 1266	1241
Co(PicO)$_3$,H_2O ………	0	35	1658sh	1639	1357 1340	1277sh † 1267	1245
Fe(PicO)$_3$ ……………	5·88		1653sh	1634	1333	1271 1261	1238
Fe(PicO)$_3$(PicOH) …	5·98	7	1709	1652	1335	1264b	1239
Fe(PicO)$_2$OMe ………	5·09	—	1686sh	1644	1333	1266	1244
Group *A* ……………				ν_1 1615—1634	ν_2 1376—1393	ν_3 1272—1282	ν_4 1230—1250
Group *B* ……………				1634—1658	1330—1357	1259—1271	1230—1247

* Sample kindly provided by Dr. A. Heller. † Non-bonded amine oxide; sh = shoulder. ‡ Conductivity (ohm^{-1} mole^{-1} cm.$^{-2}$) of 0·0005M-solutions in methanol.

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[10] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

[11] Duval, Gerding, and Lecomte, *Rev. Trav. chim.*, 1950, **69**, 391; Douville, Duval, and Lecomte, *Bull. Soc. chim. France*, 1942, **9**, 548.

[12] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

[13] Nakamoto, Morimoto, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 4528.

[14] Sievers and Bailar, *Inorg. Chem.*, 1962, **1**, 174.

binding should be about 1650 cm.$^{-1}$, and both groups have tried to correlate the position of this band with the degree of covalency in the metal–oxygen bond. Attempts have also been made to link this frequency with the electronegativity of the metal.[15] It has also been shown [13] that, as the " asymmetric " frequency increases, the corresponding " symmetric " frequency decreases, taking on more single-bond character.

When, as in (Id), a metal is bonded to each oxygen atom, the absorption becomes more like that observed for the free carboxylate ion, with consequent increase in the " symmetric " and a decrease in the " asymmetric " frequency, *e.g.*, $Cu_2(OAc)_4,2H_2O$ has absorption [12] at 1603 and 1418 cm.$^{-1}$. Moreover, if one of the metals in (Id) is replaced by a hydrogen bond to water (Ie), a similar result is obtained, the two oxygen atoms behaving as though they were equivalent, *e.g.*, $Ni(OAc)_2,4H_2O$ has absorption [12] at 1530 and 1418 cm.$^{-1}$, this complex acetate having two equal carbon–oxygen bond lengths.[16]

The complexes can be divided into two groups (Table 1) on the basis of (*a*) the energy of the high-frequency carboxyl band ν_1, (*b*) the energy of the lower-frequency carboxyl band ν_2, or (*c*) the energy of the higher-frequency amine oxide vibration ν_3; the same division is effected irrespective of which absorption is chosen. Most of the hydrates belong to the first group (A) and it seems reasonable that a structure (Ie) is present in these cases.

The second group (B) are mostly anhydrous complexes and their properties can be readily explained in terms of a structure (Ic) where the unbonded oxygen atom has high ketonic character. From the above discussion we conclude that type (Id and e) compounds should have ν_1 near 1600 cm.$^{-1}$ and ν_2 near 1400 cm.$^{-1}$, whilst those of type (Ic) should have ν_1 above 1610 cm.$^{-1}$ and ν_2 below 1400 cm.$^{-1}$ as observed.

We can, therefore, divide the complexes structurally into those having hydrogen-bonded systems with roughly equivalent carboxyl-oxygen atoms, and those having essentially a monodentate carboxyl group containing non-equivalent oxygen atoms. However, the ν_1 frequencies of group B are fairly high, and this, according to Sievers and Bailar, indicates considerable covalent binding. Also, the ν_3 amine oxide frequencies of the second group are considerably lower than those of the first. This may also be interpreted in terms of enhanced covalent bonding between the metal and the amine oxygen atom.

Group B complexes are therefore regarded as having strong covalent bonds between metal and oxygen, whilst those of group A have essentially an ionic bond between the metal and oxygen. The high ν_2 frequencies of group A are not, therefore, necessarily due to the presence of a hydrogen near the ketonic oxygen atom but rather to the enhanced ionic character of the carboxyl group that makes the oxygen atoms equivalent.

Group B contains mainly tervalent ions or bivalent ions, such as beryllium and copper, where strong covalent binding may be expected (cf. copper acetylacetonate). Beryllium, though not a transition element, gives a strongly polarising cation. Other bivalent ions are found in group A. However, it should be noticed that even here the ν_1 frequencies are above the normal ionic range (1610—1550 cm.$^{-1}$), so that some covalent character must be attributed to the group A complexes, particularly those with the higher frequencies.

In the corresponding EDTA complexes of the group A metals the ν_1 frequencies lie well within the ionic range.[14] There is therefore a profound difference in bond character between the two classes of compound. This may be due to the presence of a six-membered ring in the amine oxide case in which, at least potentially, the covalent character may be stabilised by resonance. No such possibility exists for the five-membered ring in the EDTA compounds. In this respect our complexes are analogous to the acetylacetonates.

Finally we note that the ν_4 frequency does not vary much from compound to compound, whilst the ν_3 frequency varies significantly. Only one $N^+–O^-$ stretching frequency

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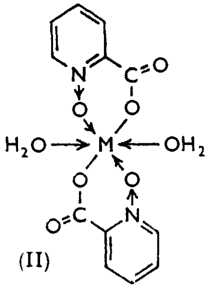
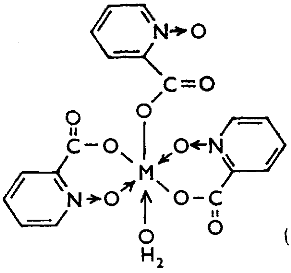
[15] Kagarise, *J. Phys. Chem.*, 1955, **59**, 271; Stimpson, *J. Chem. Phys.*, 1954, **22**, 1942.

[16] Van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 609.

is expected in 2-substituted pyridine oxides. Two bands were tentatively assigned by Katritzky and Hands[9] to the $N^+–O^-$ stretching vibration with the suggestion that the lower-frequency band was the primary stretching vibration. Our studies suggest that only the higher-frequency band is a true amine oxide vibration.

Complexes.—Inner salts of the bivalent ions may be prepared by reaction of the ligand or its ammonium salt with metal acetates. The complexes so formed have the general formula $M^{II}(PicO)_2,2H_2O$, where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Mg(II), or Zn(II). In the zinc complex 1½ mol. of water per zinc atom are present. The complexes are, in most cases, soluble in water, acetic acid, and methanol but insoluble in most other solvents. They are all non-electrolytes.


(II)


(III)

The magnetic and visible spectral data are given in Tables 1 and 2. For nickel(II) and cobalt(II), these are consistent with an octahedral configuration about the metal ion (see below). *X*-Ray powder patterns indicate that the Mn(II), Fe(II), Co(II), and Ni(II) derivatives are isomorphous. We conclude that these complexes are octahedral and probably have a structure of the type (II). In the zinc complex the metal atom is probably tetrahedrally co-ordinated but may be five-co-ordinate.[17] The powder pattern of the

TABLE 2.

Ultraviolet and visible absorption spectra: $\lambda_{max.}$ (mμ) (log ε).*

	a	*b*	*c*	*d*
PicOH	265(3·85)	314(3·08)		
$Ca(PicO)_2$	[1]258(4·30)			
$Mg(PicO)_2,2H_2O$	[1]259(4·29)			
$Mn(PicO)_2,2H_2O$	265(4·17)		405(2·45)	
$Fe(PicO)_2,2H_2O$	262(4·18)		475(2·43)	795(1·34)
$Co(PicO)_2,2H_2O$	262(4·11)		420sh(2·10)	490(1·38), 510(1·38
$Ni(PicO)_2,2H_2O$			[2]410b	680, 725
$Cu(PicO)_2,2H_2O$			[2]375sh	715, 900sh, 970sh
$Zn(PicO)_2,1\frac{1}{2}H_2O$	[1]261 (4·28)			
$Cu(PicO)_2$			[2]363sh	705, 720
$Be(PicO)_2$ †	[1]257(4·12)			
$Cr(PicO)_3,H_2O$	[1]258(4·36)	290sh(3·96)		410(2·14), 570(2·02)
$Mn(PicO)_3$	262b(4·33)			430(2·34), 485sh(2·30), 705sh(1·62), 790(1·63), 825sh(1·62)
$Co(PicO)_3,H_2O$	250b(4·50)	300sh(4·15)		415(2·48), 615(2·33), 900(0·70)
$Fe(PicO)_3$	253b(4·24)	302sh(3·66)		
$HFe(PicO)_4$	245b(4·56)	302sh(4·16)		

* Spectra in methanol solution except where numbered; (1) water; (2) diffuse reflectance spectra.
† Sample kindly provided by Dr. A. Heller.

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[17] Lippert and Truter, *J.*, 1960, 4996.

copper complex differs somewhat from those of the other complexes and, like most six-co-ordinate copper complexes, this one also probably has tetragonal distortion along the copper–water axis. All these complexes have their "symmetric" CO_2^- stretching frequency in the region of 1380 cm.$^{-1}$, there being hydrogen bonding between the carbonyl group and the hydrogen of an adjacent water molecule.

The water in these complexes is held very tenaciously, but the compound $Cu(PicO)_2,2H_2O$ may be dehydrated at 100°/15 mm.; the infrared spectrum of the resulting $Cu(PicO)_2$ is in agreement with its formulation as a simple monomeric square-planar derivative. The calcium complex $Ca(PicO)_2$, the infrared spectrum of which indicates the presence of two equivalent carboxyl-oxygen atoms, is probably polymeric and octahedral (type Id). The alternative interpretation of a purely ionic lattice is ruled out by the comparatively high "asymmetric" frequency indicative of some covalent character.

Amine oxides are oxidising agents, so that we might expect to be able to stabilise high oxidation states with this ligand. Experimentally it is observed that the bivalent manganese, iron, and cobalt compounds are readily oxidised to the tervalent state. The ferrous complex is stable in the solid state, but methanol solutions readily absorb atmospheric oxygen. Attempts to prepare a chromous derivative failed, since the reaction of chromous acetate with the ligand goes straight to the chromic state, affording $Cr(PicO)_3,H_2O$ even under an inert atmosphere. Oxidation of the manganous derivative with bromine gave a complex $Mn(PicO)_3$; the corresponding iron compound must be prepared from ferric sulphate, since oxidation by halogen leads to halogen-substituted products[18] such as $FeCl_2(PicO)$. Oxidation of the cobaltous derivatives with chlorine gave a low yield of $Co(PicO)_3,H_2O$, the main product[18] in this reaction being the bivalent-cobalt complex CoCl(PicO). The chromium and the cobalt complex are stable in cold water, but the manganese and the iron compound are hydrolysed very readily. The cobalt complex does not oxidise potassium iodide in solution at room temperature, but does so at higher temperatures.

The complexes $M(PicO)_3,H_2O$ (M = Cr or Co) cannot be dehydrated without decomposition. They show multiple $N^+{-}O^-$ frequencies suggestive of at least two kinds of $N^+{-}O^-$ bonds. Structure (III) seems feasible. The complexes of formula $M(PicO)_3$ (M = Mn or Fe) may involve simple monomeric octahedra; however, since they also show multiple $N^+{-}O^-$ bands, a polymeric system based upon the anhydrous form of (III) is a possibility. In this case, two ligand units will chelate to the metal atom whilst the third bridges successive metal atoms in the lattice. The complex $HFe(PicO)_4$ with its broad infrared and ultraviolet spectra may also be based upon (III), with the water molecule replaced by a second monodentate ligand group in its acid form.

All these complexes are non-electrolytes, but nevertheless solutions of them, with cation-precipitating agents such as ammonium reineckate, sodium tetraphenylborate, etc., give precipitates of unknown composition. Extensive rearrangement is believed to take place during this reaction.

Oxidation of the cobalt(II) and nickel(II) derivatives with bromine in acetic acid led to complexes Co(OAc)(PicO)Br (μ_{eff} = 4·99 B.M., diffuse reflectance spectrum $\lambda_{max.}$ 735sh, 700, 670, 645sh, 540 mμ) and Ni(OAc)(PicO)Br (μ_{eff} = 3·9 B.M., diffuse reflectance spectrum $\lambda_{max.}$ 730 mμ). The complexes have the unusual property of reacting instantly with water, releasing bivalent metal ions and free molecular bromine. Their absorption spectra do not indicate the presence of molecular bromine in the solid. Reaction of the nickel(II) derivative with chlorine led to chlorine-substituted products of bivalent nickel.[18] The complex $Fe(PicO)_2OMe$ obtained by atmospheric oxidation of the ferrous complex in methanol has a low magnetic moment and is probably a polymer involving metal–metal interaction.

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[18] Lever, Lewis, and Nyholm, unpublished work.

Magnetic Properties.—With the exception of the cobaltic derivative which is diamagnetic, all the complexes are spin-free. The moments observed are those expected for octahedral co-ordination.[19]

Ultraviolet and Visible Absorption Spectra.—The absorption spectra which are observed may be conveniently divided into four regions: (*a*) 240—270; (*b*) 270—350; (*c*) 350—500; (*d*) above 500 mμ.

(*a*) In this region a single absorption is observed with an intensity of ~9000 per unit per mole. This absorption probably arises from a π–π^* transition in the aromatic system (cf. benzoic acid $\lambda_{\text{max.}}$ 230 mμ; ε 10,000).

(*b*) In those cases where no distinct absorption is seen in this region, the higher-frequency band tails off so broadly that it seems likely that something lies beneath it. The band seems most prominent in the unco-ordinated ligand, and in those complexes where the ligand is believed to be monodentate. In organic molecules containing oxygen conjugated to an aromatic ring, an n–π^* transition is generally observed to the low-frequency side of the π–π^* transition.[20] For the free ligand, Hata [21] has assigned this band to an n–π^* transition. It seems likely that the band we observe in the metal complexes is essentially of this type.

(*c*) A band is observed in this region for all the bivalent metal complexes of the transition ions investigated. It is absent from spectra of the ferric derivatives and, although a band does appear within this region for other tervalent-metal complexes, it is then readily assigned as a crystal-field transition. It is absent from spectra of the zinc, magnesium, and calcium derivatives. Its presence only in transition-ion complexes suggests that it is related to the incomplete *d*-electron shell. The bands are always rather broad, indicating high oscillator strength, and are therefore perhaps charge-transfer in origin. The band has the lowest frequency for the most readily oxidisable complex, namely, ferrous, and the highest for the complex oxidised with most difficulty, namely, cupric. No definite assignment can be made, but it seems reasonable to suppose that the transition is from an orbital essentially associated with the metal ion to one predominantly located on the ligand, perhaps $d_\epsilon \longrightarrow \pi^*$. A transition of this type has been assigned [22] to bands observed in the spectra of metal acetylacetonates.

(*d*) Bands within this region are ascribed to crystal-field transitions: each ion will be discussed in turn. Crystal-field bands occurring within the previous region are also discussed here.

With manganese(II) and iron(III) no crystal-field band is observed. This is not unexpected since, being from spin-free d^5-ions, the bands would have intensities of much less than 1. It appears that any such bands are swamped by the tail of the higher-frequency absorption.

Although the metal ion in the complexes is surrounded octahedrally by six oxygen atoms, the symmetry group of the molecule is not O_h. The presence of the chelate rings, and the fact that the six oxygen atoms will not necessarily be equivalent, lowers the symmetry. The complexes $\text{M(PicO)}_3\text{,H}_2\text{O}$ have C_{2v} symmetry and it is probable that Mn(PicO)_3 also has this symmetry in solution. Compounds of the type $\text{M(PicO)}_2\text{,2H}_2\text{O}$ have C_{2h} symmetry. In principle, therefore, we should assign the spectra on the basis of these symmetries. Under C_{2v} perturbation the T_{1g} and T_{2g} levels of the octahedral group split into three levels ($T_{1g} \longrightarrow A_1 + B_1 + B_2$, $T_{2g} \longrightarrow A_2 + B_1 + A_2$). In practice, in the spectra of the cobalt(III) and chromium(III) complexes, no splitting is observed and the spectra are readily assigned in terms of O_h symmetry, although it is true that some broadening of the bands is observed.

The cobalt(II) and nickel(II) derivatives do have spectra typical of octahedral

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[19] Lewis and Wilkins, " Modern Coordination Chemistry," Interscience Publ. Inc., New York, 1960.
[20] Mason, *Quart. Rev.*, 1961, **15**, 287.
[21] Hata, *Bull. Chem. Soc. Japan*, 1958, **31**, 255.
[22] Barnum, *J. Inorg. Nucl. Chem.*, 1961, **21**, 221.

co-ordination,[19] but the detail therein was not sufficiently resolved to warrant a full analysis of the spectra. Moreover, in the case of nickel, spin–orbit coupling is sufficient to render valueless the simple treatment used below. Assignments for the crystal-field bands of the other ions are listed in Table 3.

The spectrum of the chromium(III) complex is, as previously mentioned, typical of octahedral co-ordination [19,23] and is readily assigned. The spectrum of the cobaltic derivative is typical of the diamagnetic cobalt(III) ion,[23] which has a $^1A_{1g}$ ground state. The two higher-frequency bands are readily assigned as the $^1T_{1g} \longleftarrow {}^1A_{1g}$ and $^1T_{2g} \longleftarrow {}^1A_{1g}$ transitions. The band observed at 900 mμ could arise from either the $^3T_{1g}(D) \longleftarrow {}^1A_{1g}$ or the $^3T_{2g}(D) \longleftarrow {}^1A_{1g}$ transition. In Table 3 the energies of the levels concerned are expressed in terms [23] of the crystal-field splitting parameter Dq and the Racah parameters B and C. For the 900 mμ band, it is possible to solve the simultaneous equations which are produced by assuming the former assignment; with the latter it is not. We conclude, therefore, that the 900 mμ band arises from the $^3T_{1g}(D) \longleftarrow {}^1A_{1g}$. For the manganese(III) complex, two bands near 450 mμ are observed with a separation of 2600 cm.$^{-1}$. Although this splitting might arise because of the C_{2v} symmetry of the molecule, the absence of any such splitting in the preceding cases makes this unlikely. More probably the splitting arises from a Jahn–Teller [19] distortion of the T_{2g} excited state. It is probably a reasonable approximation to assume that the mean frequency of the two bands corresponds to $10Dq$ (Table 3). The lower-frequency manganese(III) band, which is very broad, is not readily assigned. The $^3T_{1g} \longleftarrow {}^5E_g$ transition in Mn(Oxalate)$_3$ occurs [23] at 10,300 cm.$^{-1}$. If we assume that the band we observe arises from this transition and assume further that γ (C/B, the ratio of the Racah parameters) remains at its free-ion value, the value of B which is derived is higher than the free-ion value. It is probable that the band arises from some cause other than the spin-forbidden $^3T_{1g} \longleftarrow {}^5E_g$ transition.

TABLE 3.

Crystal-field assignment data.

Ion	d^n	Assignment	Energy *	ν (found)	Dq	B	$\beta = B'/B$
Cr(III)	d^3	$^4T_{2g} \longleftarrow {}^4A_{2g}$	$10Dq$	17,550	1755	570	0·62
		$^4T_{1g} \longleftarrow {}^4A_{2g}$	$10Dq + 12B$	24,400	(1740)		
Mn(III)......	d^4	$^5T_{2g} \longleftarrow {}^5E_g$	$10Dq$	21,300 †	2130		
		$^3T_{1g} \longleftarrow {}^5E_g$	$6B - 10Dq + 5C$	12,900?	(2100)		
Co(III)	d^6	$^3T_{1g} \longleftarrow {}^1A_{1g}$	$10Dq - 3C$	11,100	1890	486 ‡	0·46
		$^1T_{1g} \longleftarrow {}^1A_{1g}$	$10Dq - C$	16,300	(1910)		
		$^1T_{2g} \longleftarrow {}^1A_{1g}$	$10Dq + 16B - C$	24,100			
Fe(II)	d^6	$^5E_g \longleftarrow {}^5T_{2g}$	$10Dq$	12,550	1255		
					(1040)		

* C. K. Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p. 74. † Mean frequency of double band. ‡ $C = 2600$ cm.$^{-1}$ (found). Values in parentheses below Dq column are Dq values for the corresponding hexahydrates (references in text). The energy equations quoted, involving the Racah parameters B and C, are those corresponding to the ground-state = zero.

Broad absorption in the 800 mμ region in the case of the ferrous complex may be attributable to the $^5E_g \longleftarrow {}^5T_{2g}$ transition. For Fe(H$_2$O)$_6^{2+}$ an absorption is assigned to this transition [24] at about 10,400 cm.$^{-1}$. However, the broadness of the band and its somewhat high energy may indicate considerable splitting as a result of the C_{2h} symmetry.

In general, the value of Dq which is obtained is similar to that present in the corresponding hexahydrates, *i.e.*, the field of the bidentate ligand is roughly equivalent to the field of two water molecules. We may tentatively place this ligand adjacent to water in the spectrochemical series.

[23] Jørgensen, " 10me Conseil de Chimie Solvay," Stoops, Brussels, 1956, p. 355.

[24] Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1502.

The value of β [the ratio of the interelectronic repulsion parameter (B') in the complex, to that (B) in the gaseous ion] which we have evaluated in two cases (Table 3) is appreciably less than those observed for the corresponding hexahydrates [25] and is comparable with those observed for the corresponding hexacyanides.[25] The value of β may be related to the degree of delocalisation of the central-ion electrons into ligand orbitals and/or the covalent character in the bond.[25] The comparatively low values we observe therefore represent further evidence for the high degree of covalent character believed to be present in the metal–oxygen bonds. The values of β we observe enable us tentatively to place this ligand adjacent to the cyanide ion in the nephelauxetic series.

EXPERIMENTAL

The infrared spectra were measured with a Grubb–Parsons G.S.2A spectrometer, and the ultraviolet and visible absorption spectra with a Unicam S.P. 500 instrument, with reflectance attachment. The magnetic measurements were made by the Gouy method, with mercury tetrathiocyanatocobaltate(II) as calibrant.[26] Carbon and hydrogen analyses were carried out in this Department by Mr. A. Winter, and nitrogen analyses by the Oxford Microanalytical Laboratory. The ligand, picolinic acid *N*-oxide, has been described previously.[27]

Di-(N-*oxido-2-picolinato*)*diaquomanganese*(II).—Aqueous solutions of ammonium picolinate *N*-oxide (2 mol.) and manganous acetate (1 mol.) were mixed and boiled for about 5 min. The yellow crystals, obtained on cooling, were recrystallised from boiling water and dried *in vacuo* (Found: C, 39·4; H, 3·5; Mn, 15·1. $C_{12}H_{12}MnN_2O_8$ requires C, 39·3; H, 3·3; Mn, 14·95%).

Di-(N-*oxido-2-picolinato*)*diaquoiron*(II).—Solutions of ammonium picolinate *N*-oxide and ferrous ammonium sulphate (stoicheiometric proportions as above) were out-gassed by nitrogen and mixed at 0°. The deep red solution, kept at 0°, deposited magenta crystals of the *complex* in high yield. These cannot be readily recrystallised without oxidation, and were washed with water and dried in a desiccator (Found: C, 38·8; H, 3·7; Fe, 15·4. $C_{12}H_{12}FeN_2O_8$ requires C, 39·1; H, 3·3; Fe, 15·2%).

Di-(N-*oxido-2-picolinato*)*diaquocobalt*(II).—Prepared in the same manner as the manganous complex, this pink crystalline *complex* may be recrystallised from water (Found: C, 39·0; H, 3·4; Co, 15·4. $C_{12}H_{12}CoN_2O_8$ requires C, 38·8; H, 3·3; Co, 15·9%).

Di-(N-*oxido-2-picolinato*)*diaquonickel*(II).—This is prepared in the same manner as the manganous complex, except that the deep green solution is maintained at 90° for several hours. During this period large green crystals of the pure *product* are obtained in high yield (Found: C, 39·0; H, 3·5; Ni, 15·8. $C_{12}H_{12}N_2NiO_8$ requires C, 38·8; H, 3·3; Ni, 15·9%).

Di-(N-*oxido-2-picolinato*)*diaquocopper*(II).—This *complex* is prepared in the same manner as the manganous complex. Recrystallisation is difficult (Found: C, 38·4; H, 2·9; Cu, 17·0; N, 7·3. $C_{12}H_{12}CuN_2O_8$ requires C, 38·4; H, 3·2; Cu, 16·9; N, 7·45%).

Di-(N-*oxido-2-picolinato*)*copper*(II).—The above diaquo-complex was heated at 120°/10 mm. for 4 hr., giving the new *product* (Found: C, 42·7; H, 2·7; Cu, 18·7. $C_{12}H_8CuN_2O_6$ requires C, 42·5; H, 2·4; Cu, 18·7%).

Di-(N-*oxido-2-picolinato*)*sesquiaquozinc*(II).—Prepared in the same manner as the manganous complex, this white *complex* may be recrystallised from water (Found: C, 39·0; H, 3·4; N, 7·4; Zn, 17·7. $C_{24}H_{22}N_4O_{15}Zn_2$ requires C, 39·1; H, 3·0; N, 7·6; Zn, 17·7%).

Di-(N-*oxido-2-picolinato*)*calcium*.—Prepared in the same manner as the manganous complex, the *calcium complex* may be recrystallised from water, from which it is obtained anhydrous (Found: C, 45·8; H, 2·8; Ca, 12·6. $C_{12}H_8CaN_2O_6$ requires C, 45·6; H, 2·5; Ca, 12·7%).

Di-(N-*oxido-2-picolinato*)*diaquomagnesium*.—The *magnesium complex* was prepared in the same manner as the manganous complex. Recrystallisation is best effected from 1 : 1 acetone–water (Found: C, 42·6; H, 4·0; Mg, 7·6. $C_{12}H_{12}MgN_2O_8$ requires C, 42·9; H, 3·6; Mg, 7·2%).

Tri-(N-*oxido-2-picolinato*)*aquochromium*(III).—Chromous acetate (1 mol.) and an aqueous solution of ammonium 2-picolinate oxide (3 mol.) were refluxed under nitrogen for 1 hr. The

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[25] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

[26] Figgis and Nyholm, *J.*, 1958, 4190.

[27] Diels, Alder, Friedrichsen, Klare, Winkler, and Schrum, *Annalen*, 1933, **505**, 103.

violet solution of the *chromic complex* obtained was set aside at room temperature for several days. The violet crystals deposited were recrystallised from a small volume of boiling water (Found: C, 44·9; H, 3·2; Cr, 10·6. $C_{18}H_{14}CrN_3O_{10}$ requires C, 44·6; H, 2·9; Cr, 10·7%).

Tri-(N-*oxido-2-picolinato*)*manganese*(III).—Picolinic acid oxide (2 equiv.—the use of the stoicheiometric three equiv. suppresses the bromine oxidation reaction entirely, the manganese being recovered in the bivalent state) and manganous acetate (1 mol.), dissolved in a sufficient volume of glacial acetic acid to maintain a clear solution at 90°, were treated at 90° with bromine (4 mol.). The deep red-brown liquid was kept at this temperature and allowed to evaporate until a viscous brown oil was left. The oil was taken up in boiling methanol containing a few drops of acetic acid and then cooled in ice. Reddish-brown crystals of the *complex* were obtained and were washed with ether and dried in a desiccator (Found: C, 46·2; H, 3·0; Mn, 11·4; N, 8·6. $C_{18}H_{12}MnN_3O_9$ requires C, 46·1; H, 2·6; Mn, 11·7; N, 8·95%).

Tri-(N-*oxido-2-picolinato*)*iron*(III).—Aqueous solutions of ammonium 2-picolinate oxide and ferric ammonium sulphate were mixed in stoicheiometric proportion, hydrolysis in the latter solution being suppressed by the addition of a few drops of 2N-sulphuric acid (N.B. too concentrated acid prevents complex formation), and the yellow solution obtained was left in a refrigerator overnight. The yellow crystalline *complex* was washed with water and dried in a desiccator. Recrystallisation may be effected from very dilute sulphuric acid (*ca.* 0·05N) (Found: C, 45·85; H, 2·8; Fe, 11·7. $C_{18}H_{12}FeN_3O_9$ requires C, 46·0; H, 2·6; Fe, 11·9%).

Hydrogen Tetra-(N-*oxido-2-picolinato*)*ferrate*(III).—Ferric chloride (0·75 g.) and picolinic acid oxide (1·93 g.) were refluxed in glacial acetic acid (25 ml.) for 1 hr. After evaporation at 90°, the yellow oil which remained was extracted rapidly with boiling ethanol. The greenish-yellow crystals obtained on cooling were washed with ether and dried in a desiccator (Found: C, 47·7; H, 3·0; Fe, 9·6. $C_{24}H_{16}FeN_4O_{12}$ requires C, 48·1; H, 2·8; Fe, 9·3%).

Methoxydi-(N-*oxido-2-picolinato*)*iron*(III).—A methanol solution of the ferrous complex above was shaken with oxygen or air. Oxygen uptake is rapid, the red solution becoming yellow and depositing crystals of the insoluble *ferric complex* (Found: C, 43·1; H, 3·6; Fe, 15·6. $C_{13}H_{11}FeN_2O_7$ requires C, 43·0; H, 3·0; Fe, 15·4%).

Tri-(N-*oxido-2-picolinato*)*aquocobalt*(III).—Cobalt acetate (1·5 g.) and picolinic acid oxide (2·52 g.) in glacial acetic acid (50 ml.), when treated with chlorine at 70° for 2 hr., yielded a green-blue *product* which recrystallised from boiling methanol. Hygroscopic green crystals (0·35 g., 9%) were obtained (Found: C, 43·9; H, 3·0; Co, 11·8. $C_{18}H_{14}CoN_3O_{10}$ requires C, 44·0; H, 2·9; Co, 12·0%).

Bromoacetato-(N-*oxido-2-picolinato*)*cobalt*.—A stirred glacial acetic acid solution (50 ml.) of cobalt acetate (1 g.) and 2-picolinic acid oxide (1·12 g.) was treated dropwise with bromine (0·65 g., 2 mol. in acetic acid, 10 ml.) at 70°. The yellow precipitate, coloured by an excess of bromine, was washed with acetic acid and ether and transferred rapidly to a vacuum-desiccator. The grey *complex* (1·0 g.) (Found: C, 28·2; H, 2·4; Br, 23·8; Co, 17·3, 17·8; N, 4·3. $C_8H_7BrCoNO_5$ requires C, 28·6; H, 2·1; Br, 23·8; Co, 17·5; N, 4·2%) decomposes in water or moist air, yielding cobalt(II) ions and molecular bromine.

Bromoacetato-(N-*oxido-2-picolinato*)*nickel*.—Prepared in the same manner as above, the nickel complex was pale yellow and impure; it was not readily purified. It yielded bromine in contact with water. The two complexes gave virtually superimposable infrared spectra.

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