

452. *Transition-metal Halide–Methyl Cyanide Complexes. Part I.
Manganese, Cobalt, and Nickel.*

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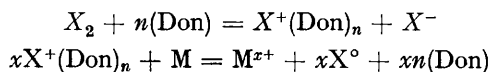
Methyl cyanide forms complexes with manganese, cobalt, and nickel either by recrystallisation of anhydrous halides from methyl cyanide or by reactions of the metals with halogens in methyl cyanide solution. Manganese and nickel chlorides and bromides form octahedral complexes, $\text{MX}_2 \cdot 2\text{MeCN}$; while cobalt forms tetrahedral complexes $\text{CoX}_2 \cdot 3\text{MeCN}$, which contain a mole of unco-ordinated methyl cyanide, and which give $\text{CoX}_2 \cdot 2\text{MeCN}$ when pumped under vacuum. The iodides of all three metals form complexes $\text{MI}_2 \cdot 3\text{MeCN}$, which are formulated as $[\text{M}(\text{MeCN})_6]^{2+}[\text{MI}_4]^{2-}$. The formation of $[\text{MI}_4]^{2-}$ ions is probably dominated by the polarisability of the iodide ion and the high degree of covalent bonding associated with this anion, whereas the formation of tetrahedral cobalt chloride and bromide complexes is determined by the stable $e^4t_2^3$ electron configuration. The reaction of these metals with bromine in methyl cyanide gives a series of complexes $[\text{M}(\text{MeCN})_6]^{2+}(\text{Br}_3^-)_2$, although only the nickel complex is stable. Evidence for the structures of these complexes has been sought from their reflectance spectra and magnetic properties. The splitting of the ${}^3T_{2g}(F)$ level in nickel(II) by non-equivalent ligands and the position of methyl cyanide in the spectrochemical series are discussed.

THE co-ordinating ability of methyl cyanide has previously been examined with transition-metal ions in the presence of the very weakly co-ordinating tetrafluoroborate¹ and perchlorate² anions where methyl cyanide occupies all the octahedral co-ordination sites round the metal ion, *e.g.*, in $[\text{Co}(\text{MeCN})_6](\text{BF}_4)_2$. This Paper is a more detailed account of

¹ Hathaway, Holah, and Underhill, *J.*, 1962, 2444.

² Hathaway and Underhill, *J.*, 1961, 3091.

studies, which we previously reported briefly,³ on the co-ordinating ability of methyl cyanide in the presence of strong co-ordinating anions, such as halide ions, where there is competition between the halides and methyl cyanide for metal co-ordination sites. The work has been approached from two directions, (1) dissolution of anhydrous halides in methyl cyanide, and (2) reactions of transition metals with halogens in methyl cyanide. The latter reaction is analogous to the reaction between metals and NOBF_4 ,¹ and can be summarised as



EXPERIMENTAL

The methyl cyanide was dried and purified by fractional distillation from phosphorus pentoxide, and the anhydrous halides MnCl_2 , MnBr_2 , CoCl_2 , CoBr_2 , CoI_2 , NiCl_2 , and NiBr_2 were prepared by pumping the hydrates under vacuum for 24 hr. at 100–140°.

Preparation of Complexes.—(a) *Anhydrous halides in methyl cyanide.* Cobalt halides were dissolved in methyl cyanide (15 ml.), and the hot saturated solution was filtered through a No. 3 sintered-glass filter-stick protected from the atmosphere by phosphorus pentoxide guard tubes.⁴ Crystals of the complex, which appeared on cooling, were filtered off, washed with methyl cyanide (1–2 ml.), and dried under vacuum.

Because of their low solubilities in methyl cyanide, the manganese and nickel halides (3 g.) were extracted in a Soxhlet apparatus with methyl cyanide (50 ml.). The complexes formed in the flask were filtered off, washed, and dried as above.

(b) *Reactions of metals and halogen in methyl cyanide.* Chlorine was passed into a suspension of manganese cobalt, or nickel (2 g.) in methyl cyanide (50 ml.), protected from moisture. Manganese and cobalt reacted extremely slowly and the crystals which formed were re-dissolved by heating the solution; hot filtration and subsequent isolation of the complexes were carried out as above. Nickel sheet reacted quickly, forming a mass of small crystals. Unchanged metal was removed and the unstable complex isolated.

The reactions between the metals (2 g.) and bromine (2 ml.) or iodine (1–2 g.) in methyl cyanide (15 ml.) were carried out in a tube fitted with a condenser and guard tube. The hot solutions were filtered (a) when the reactions of bromine and iodine were complete (as indicated by the clear colour of the methyl cyanide dripping back from the condenser) or (b) when the reactions were incomplete. Products were isolated as above.

Table 1 lists the complexes isolated along with their colours, methods of preparation, and analyses.

Analysis.—The metals were analysed according to the methods given by Vogel,⁵ the halides gravimetrically as silver halide, and the free halogen by titration with thiosulphate after addition of excess of potassium iodide. The results are recorded in Table 1.

Physical Properties.—Infrared and reflectance spectra,⁶ room temperature magnetic moments,⁶ X-ray powder diffraction patterns,¹ and electrical conductivities¹ were measured as previously described.

Infrared Spectra.—The i.r. spectrum of methyl cyanide in the region 2000–2400 cm^{-1} consists of a sharp intense band at 2255 cm^{-1} , assigned to the $\text{C}\equiv\text{N}$ fundamental stretch, and a weak band at 2293 cm^{-1} , assigned to a combination of the C–C stretch and the CH_3 deformation.⁷ In co-ordination compounds of methyl cyanide two very strong bands appear at slightly higher wave-numbers and these have been assigned as in the free solvent.⁸ However, it may be possible for the two strong bands to arise through a splitting of the fundamental $\text{C}\equiv\text{N}$ stretch through coupling, leaving the weak combination band hidden beneath the more intense absorptions. The i.r. spectra of phenyl cyanide lacks the combination band and shows the $\text{C}\equiv\text{N}$ stretch at 2250 cm^{-1} which is shifted and appears as a single band at 2285 cm^{-1} in co-ordination compounds such as $[\text{Ni}(\text{PhCN})_6](\text{BF}_4)_2$.⁹ This rules out coupling and verifies the

³ Hathaway and Holah, *VII I.C.C.C. Abstracts*, 1962, 47.

⁴ Addison and Hathaway, *J.*, 1960, 1468.

⁵ Vogel, "Textbook of Quantitative Inorganic Analysis," Longmans, Green, and Co., London.

⁶ Hathaway, Holah, and Hudson, *J.*, 1963, 4586.

⁷ Venkatesarlu, *J. Chem. Phys.*, 1951, 19, 293.

⁸ Clark, Lewis, Machin, and Nyholm, *J.*, 1963, 379.

⁹ Elliott, Hathaway, and Holah, unpublished work.

original assignments in co-ordinated methyl cyanide.⁸ It is surprising that the combination band appears with such a strong intensity, but as both the combination band and the C≡N stretching vibration have A_1 symmetry the former may gain intensity from the latter by Fermi resonance.

TABLE I.
Complexes, preparations, and analyses.

	Preparative route	Colour	Found (%)			Required (%)		
			Metal	Halide	Halogen	Metal	Halide	Halogen
MnCl ₂ ,2L	1, 2	pink	26.3	34.1	—	26.4	34.1	—
MnBr ₂ ,2L	1, 2	pink	18.45	53.9	—	18.5	53.8	—
MnBr ₂ ,6L,2Br ₂ *	3	red	7.7	41.1	40.4	7.0	40.9	40.9
MnI ₂ ,3L	2	yellow	12.9	58.8	—	12.7	58.8	—
CoCl ₂ ,3L †	1, 2	blue	23.2	28.0	—	23.3	28.0	—
CoCl ₂ ,2L †	4	blue	27.75	33.55	—	27.8	33.5	—
CoBr ₂ ,3L †	1, 2	blue	17.2	46.65	—	17.2	46.7	—
CoBr ₂ ,2L †	4	blue	19.45	53.2	—	19.6	53.1	—
CoBr ₂ ,6L,2Br ₂ *	3	brown	6.85	41.0	43.1	7.5	40.7	40.7
CoI ₂ ,3L	1, 2	green	13.5	58.2	—	13.5	58.2	—
NiCl ₂ ,2L	1	yellow-green	27.6	33.5	—	27.7	33.5	—
NiCl ₂ ,4L	2	green	19.7	24.1	—	20.0	24.1	—
NiBr ₂ ,2L	1	blue-green	19.4	53.1	—	19.5	53.2	—
NiBr ₂ ,6L,2Br ₂ ...	2	brown	7.3	40.6	40.8	7.5	40.75	40.75
NiI ₂ ,3L	2	red	13.35	58.35	—	13.5	58.3	—

L = Methyl cyanide.

Preparative route: 1, anhydrous halide in methyl cyanide; 2, reaction of metal with halogen in methyl cyanide (complete); 3, as 2, incomplete; 4, complexes from methods 1 and 2 pumped under vacuum at room temperature for 5 hr.

* Very unstable with respect to loss of bromine. † Previously prepared^{19,20} but as ref. 19 claimed the bis(methyl cyanide) complexes and ref. 20 the tris-complexes, the analysis for both series is included to confirm that both series exist.

The i.r. spectra of the complexes under discussion are recorded in Table 2 and show the presence of co-ordinated methyl cyanide in all cases, with some unco-ordinated solvent in the case of two cobalt complexes, which will be discussed later.

TABLE 2.
Infrared spectra and magnetic data.

	Infrared spectra (cm. ⁻¹)	Magnetic moments (μ , B.M.)	
		obs.	r.m.s.
MnCl ₂ ,2L	— 2275 2295	5.83	
MnBr ₂ ,2L	— 2270 2295	5.79	
MnI ₂ ,3L	— 2275 2295	5.86	?
CoCl ₂ ,3L	2255 2280 2302	4.86	4.89
CoCl ₂ ,2L	— 2285 2310	4.80	
CoBr ₂ ,3L	2255 2280 2300	4.88	4.94
CoBr ₂ ,2L	— 2275 2295	4.84	
CoI ₂ ,3L	— 2275 2290	5.02	4.97
NiCl ₂ ,2L	— 2280 2300	3.47	
NiCl ₂ ,4L	2255 2280 2300	—	
NiBr ₂ ,2L	— 2280 2302	3.40	
NiBr ₂ ,6L,2Br ₂	— 2285 2303	3.23	
NiI ₂ ,3L	— 2283 2304	3.36	3.32

Manganese Complexes.—The manganese chloride and bromide complexes are pale pink, strongly suggestive of octahedral co-ordination, which is supported by their reflectance spectra (Fig. 1 and Table 3). Because all $d-d$ bands are both spin and Laporte forbidden they are difficult to study by reflectance spectroscopy, and in fact very few complexes have been examined. The assignments in Table 3 were made by comparisons with the solution spectrum of $[\text{Mn}(\text{H}_2\text{O})_6^{2+}]$ ¹⁰ and the band widths are in good agreement with the order predicted by

¹⁰ Dunn, "Modern Coordination Chemistry," Ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 229.

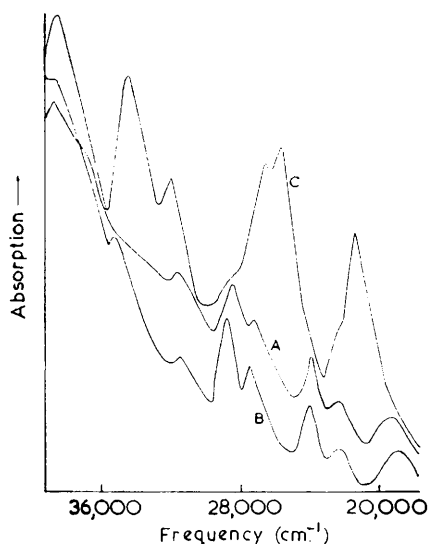


FIG. 1. The reflectance spectra of some solid manganese(II) complexes.

A, $\text{MnCl}_2 \cdot 2\text{MeCN}$; B, $\text{MnBr}_2 \cdot 2\text{MeCN}$;
C, $\text{MnI}_2 \cdot 3\text{MeCN}$.

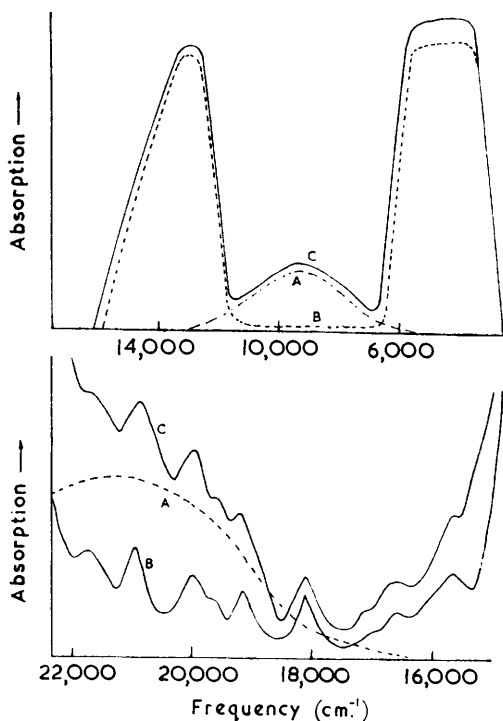


FIG. 2. The reflectance spectra of some solid cobalt(II) complexes.

A, $\text{Co}(\text{MeCN})_6(\text{BF}_4)_2$; B, $[\text{Et}_4\text{N}]_2[\text{CoI}_4]$;
C, $\text{CoI}_2 \cdot 3\text{MeCN}$.

TABLE 3.

	Electronic reflectance spectra (cm^{-1}).									
	${}^4T_1(G)$	${}^4T_2(G)$	${}^4E, {}^4A(G)$	${}^4T_1(D)$	${}^4E(D)$	${}^4T_1(P)$	${}^4A_2(F)$	${}^4T_1(F)$	${}^4T_2(F)$	
$\text{MnCl}_2 \cdot 2\text{L}$	19,000	22,400	23,800	27,200	28,550	31,200	35,000	37,700		
$\text{MnBr}_2 \cdot 2\text{L}$	19,200	22,200	23,800	27,000	28,200	31,200	36,700	38,000		
$\text{MnI}_2 \cdot 3\text{L}$		21,250	22,200	25,800	26,700	28,200	32,100	34,400	38,700	
		${}^4T_1(F)$			${}^4T_1(P)$					
$\text{CoCl}_2 \cdot 3\text{L}$	5000	7120		15,100	16,800					
$\text{CoCl}_2 \cdot 2\text{L}$	4540	4570	5400	14,100	14,900	16,400				
			6260							
$\text{CoBr}_2 \cdot 3\text{L}$	4440	6900		14,800	15,700					
$\text{CoBr}_2 \cdot 2\text{L}$	5640	7020	8760	14,300	17,000					
$\text{CoI}_2 \cdot 3\text{L}$	4160	5000	9260*	13,000	13,450					
		${}^3T_{2g}(F)$								
		${}^3B_{2g}$	3E_g	$1E_g(D)$	${}^3T_{1g}(F)$	${}^1T_{2g}(D)$	${}^3T_{1g}(P)$			
$\text{NiCl}_2 \cdot 2\text{L}$		6600	8250	12,300	13,700	19,400	23,700			
$\text{NiBr}_2 \cdot 2\text{L}$		6600	8250	12,500	14,000	19,600	23,000			
$\text{NiBr}_2 \cdot 6\text{L} \cdot 2\text{Br}_2$			10,750	13,800	17,200	—	—			
$\text{NiL}_6(\text{BF}_4)_2$			10,700	13,900	17,400	—	—			27,800
		${}^3T_2(F)$	${}^3A_2(F)$	1D	${}^3T_1(P)$	1G				
$\text{NiI}_2 \cdot 3\text{L}$		—	7140	—	11,400—11,900	13,900				

* ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ transition in octahedral $[\text{Co}(\text{CH}_3\text{CN})_6^{2+}]$.

Orgel.¹¹ The magnetic moments are consistent with spin-free manganese(II). The most likely structure of these solids consists of chains of octahedrally co-ordinated manganese atoms with bridging halide ions in the *xy* plane with two methyl cyanide ligands in the *z* direction.

The bright yellow colour and intense reflectance spectrum of $\text{MnI}_2 \cdot 3\text{MeCN}$ (Fig. 1) is strongly suggestive of tetrahedral manganese(II)¹² and the complex is formulated as $[\text{Mn}(\text{MeCN})_6^{2+}][\text{MnI}_4^{2-}]$. Because of the intensity of the $[\text{MnI}_4^{2-}]$ spectrum, none of the bands due to $[\text{Mn}(\text{MeCN})_6^{2+}]$ are observed. The magnetic moment (Table 2) is consistent with, but does not prove, the structure. The complex is a 1 : 1 electrolyte in 0.1M-solution in methyl cyanide, having a conductance of 130 $\text{ohm}^{-1} \text{cm}^2$ compared with 150 $\text{ohm}^{-1} \text{cm}^2$ for tetraethylammonium bromide at the same concentration.¹³

Cobalt Complexes.—Cobalt(II) forms many stable pink octahedral ($t_{2g}^5 e_g^2$) and blue tetrahedral ($e^4 t_2^3$) complexes, examples being $[\text{Co}(\text{MeCN})_6](\text{BF}_4)_2$ ¹ and $(\text{Bu}^n\text{N})_2[\text{CoI}_4]$.¹⁴ The reflectance spectra of these are shown in Fig. 2, together with the reflectance spectrum of $\text{CoI}_2 \cdot 3\text{MeCN}$; assignments are recorded in Table 3. Fig. 2 shows that the iodide complex contains both $[\text{Co}(\text{MeCN})_6^{2+}]$ and $[\text{CoI}_4^{2-}]$ ions, and is therefore formulated as $[\text{Co}(\text{MeCN})_6^{2+}][\text{CoI}_4^{2-}]$. This is supported by i.r. spectral evidence, which shows all the methyl cyanide to be co-ordinated, the effective magnetic moment, which agrees with the root-mean-square moments of the constituents, and the electrical conductivity, which has a value of 135 $\text{ohm}^{-1} \text{cm}^2$ in 0.1M-solution in methyl cyanide, this being consistent with a 1 : 1 electrolyte.

The i.r. spectra of $\text{CoCl}_2 \cdot 3\text{MeCN}$ and $\text{CoBr}_2 \cdot 3\text{MeCN}$ have bands at 2255 cm^{-1} due to free methyl cyanide as well as the intense higher energy bands of the co-ordinated solvent. A mole of methyl cyanide is removed from each compound by pumping it under vacuum at room temperature for several hours. The reflectance spectra of these complexes in the near infrared, ${}^4A_2 \rightarrow {}^4T_1(F)$, and the visible, ${}^4A_2 \rightarrow {}^4T_1(P)$, regions are discussed separately, together with the reflectance spectra of $(\text{Me}_4\text{N})_2[\text{CoCl}_4]$, $\text{CoCl}_2 \cdot 2\text{Py}$, $(\text{Et}_4\text{N})_2[\text{CoBr}_4]$, and $\text{CoBr}_2 \cdot 2\text{Py}$.

The ${}^4A_2 \rightarrow {}^4T_1(F)$ bands are shown in Fig. 3, where, in the pyridine complexes, the band is resolved into two components under C_{2v} symmetry.¹⁵ $\text{CoCl}_2 \cdot 3\text{MeCN}$ and $\text{CoBr}_2 \cdot 3\text{MeCN}$ also show splitting of this band, which, assuming structures such as $[\text{CoCl}_2 \cdot 2\text{MeCN}]\text{MeCN}$, would be the result of two factors, (a) non-equivalent ligands, and (b) the odd methyl cyanide in the lattice causing distortion. When the unco-ordinated molecule is removed, the compounds appear to be slightly more regular, $\text{CoCl}_2 \cdot 2\text{MeCN}$ having a band very similar to $[\text{CoCl}_4^{2-}]$, while $\text{CoBr}_2 \cdot 2\text{MeCN}$ has distinct detail on the strong band. It is rather surprising that the bands of $\text{CoCl}_2 \cdot 2\text{Py}$ and $\text{CoCl}_2 \cdot 2\text{MeCN}$ differ so radically considering the closeness of pyridine and methyl cyanide in the spectrochemical series, $\text{I} < \text{Br} < \text{Cl} < \text{H}_2\text{O} < \text{MeCN} < \text{Py} < \text{NH}_3$. Why there should be this difference is not understood. The extensive splitting of these bands must arise from crystal fields of lower symmetry as spin-orbit coupling can only produce splitting of the order of 1000 cm^{-1} in this region.¹⁶

The ${}^4T_1(P)$ state occurs in the same region as states arising from the doublet 2G term,¹⁶ and as a result of spin-orbit coupling, the visible band ${}^4T_1(P) \leftarrow {}^4A_2$, is extremely complex. This band appears to be less influenced by the environment of the metal ion than is the ${}^4T_1(F) \leftarrow {}^4A_2$ transition,¹⁵ and all that can be said is that the strong band in the visible region in all the complexes is consistent with tetrahedral cobalt(II). No attempt has been made to interpret the spin-forbidden transitions to the doublets, since this is an extremely complex region of the spectrum of tetrahedral cobalt(II). It has been estimated that, including the effects of spin-orbit coupling and lowering of site symmetry, about 20 bands due to transitions to the 2G , 2P , 2H , 2D , and 2F states are expected between 15,000 and 30,000 cm^{-1} .¹⁶ There is no apparent correlation between the positions of the doublet transitions on the chloride and bromide complexes, although many bands are observed.

Cotton *et al.*¹⁷ prepared some dimethyl sulphoxide complexes of cobalt of formulæ $\text{CoX}_2 \cdot 3\text{DMSO}$ (where $\text{X} = \text{Cl}^-$, Br^- , and I^- , and $\text{DMSO} = \text{dimethyl sulphoxide}$), all of which

¹¹ Orgel, *J. Chem. Phys.*, 1955, **23**, 1824.

¹² Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1962, **84**, 167; Furlani and Furlani, *J. Inorg. Nuclear Chem.*, 1960, **19**, 51.

¹³ Fowles and Hoodless, *J.*, 1963, **33**.

¹⁴ Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

¹⁵ Ferguson, *J. Chem. Phys.*, 1960, **32**, 528.

¹⁶ Liehr, *J. Phys. Chem.*, 1963, **67**, 1314; Ferguson, *J. Chem. Phys.*, 1963, **39**, 116.

¹⁷ Cotton and Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986; *J. Inorg. Nuclear Chem.*, 1961, **17**, 62; Cotton, Francis, and Horrocks, *J. Phys. Chem.*, 1961, **64**, 1534.

were formulated as $[\text{Co}(\text{DMSO})_6][\text{CoX}_4]$ on the basis of the visible band and i.r. spectral evidence. In view of our findings with the methyl cyanide complexes, we have extended their reflectance measurements into the near infrared region and in fact find bands consistent with $[\text{CoX}_4^{2-}]$ ions, fully justifying the above formulation.

The effective magnetic moments of these complexes (Table 2) are consistent with those generally found for tetrahedral cobalt complexes,¹⁸ being greater than the spin-only value of 3.88 B.M. due to orbital angular momentum being "mixed into" the ground state by the 4T_2 level. Although moments of $\text{CoX}_2 \cdot 3\text{MeCN}$ all agree with root-mean-square values calculated from $[\text{CoX}_4^{2-}]$ and $[\text{Co}(\text{MeCN})_6]^{2+}$ spectral evidence has shown clearly that this structure only applies for the iodide. The moments of the chloride and bromide complexes show little change when the unco-ordinated molecule of methyl cyanide is removed.

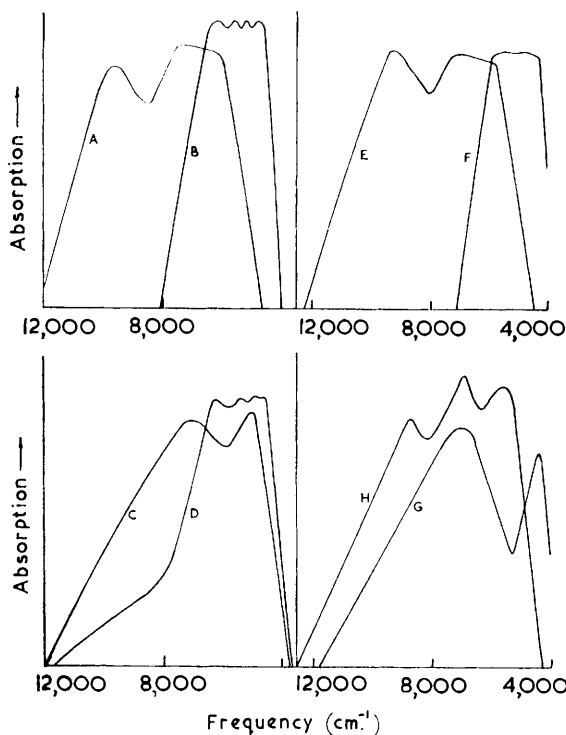


FIG. 3. The reflectance spectra of some solid cobalt(II) complexes.

- A, $\text{CoCl}_2 \cdot 2\text{py}$; B, $[\text{Et}_4\text{N}]_2[\text{CoCl}_4]$;
 C, $\text{CoCl}_2 \cdot 3\text{MeCN}$; D, $\text{CoCl}_2 \cdot 2\text{MeCN}$;
 E, $\text{CoBr}_2 \cdot 2\text{py}$; F, $[\text{Et}_4\text{N}]_2[\text{CoBr}_4]$;
 G, $\text{CoBr}_2 \cdot 3\text{MeCN}$; H, $\text{CoBr}_2 \cdot 2\text{MeCN}$.

X-Ray powder diffraction patterns were taken of the five cobalt complexes, but there appeared to be no evidence of any isomorphism between any of the complexes. This gives some support to the differences indicated by the reflectance spectra.

A study of the physical properties of these cobalt complexes with methyl cyanide enables discrepancies in the early literature to be explained. Nauman,¹⁹ and recently Marcinkowsky²⁰ isolated the complexes $\text{CoCl}_2 \cdot 3\text{MeCN}$ and $\text{CoBr}_2 \cdot 3\text{MeCN}$, while Hantzsch²¹ obtained $\text{CoCl}_2 \cdot 2\text{MeCN}$ and $\text{CoBr}_2 \cdot 2\text{MeCN}$ from similar reactions. It seems that Hantzsch used a too-rigorous method for drying the complexes and removed the unco-ordinated solvent. Marcinkowsky (and ourselves³) suggested, by studying conductivities and solution spectra in the visible region, that these two complexes are formulated as $[\text{Co}(\text{MeCN})_6][\text{CoX}_4]$, but a more detailed study has shown this not to be the case in the solid. The compounds solvolyse extensively in methyl cyanide, and it seems very unlikely that, in solution, a monomeric species $[\text{CoCl}_2 \cdot 2\text{MeCN}]\text{MeCN}$ exists to any great extent, making information obtained from conductivity measurements open to some doubt.

¹⁸ Holm and Cotton, *J. Chem. Phys.*, 1959, **31**, 788; 1960, **32**, 1168.

¹⁹ Nauman, *Ber.*, 1914, **47**, 247.

²⁰ Marcinkowsky, Ph.D. Thesis, Rensselaer Polytechnic Inst., 1961.

²¹ Hantzsch, *Z. anorg. Chem.*, 1927, **159**, 273.

Nickel Complexes.—Nickel(II), d^8 , forms many regular octahedral complexes which are generally pale yellow or green, but recently increasing numbers of bright blue or red tetrahedral complexes have been isolated. As with cobalt, typical examples are $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ ¹ and $(\text{Et}_4\text{N})_2[\text{NiI}_4]$,²² which can be distinguished by their reflectance spectra. The reflectance spectrum of $\text{NiI}_2 \cdot 3\text{MeCN}$, shown in Fig. 4, is consistent with $[\text{NiI}_4^{2-}]$ ions but in this case it is not possible to observe any bands due to $[\text{Ni}(\text{MeCN})_6]^{2+}$ (Fig. 4) since these are obscured by the intense absorptions of the tetrahedral species. The first band, ${}^3T_2(F) \leftarrow {}^3T_1(F)$, is outside the range of observation, but the second, to ${}^3A_2(F)$, is strong and sharp at 7140 cm^{-1} . The transition to the 1D state which is reported²² to occur in the spectrum of $[\text{NiI}_4^{2-}]$ is not observed here. In the visible region the strong ${}^3T_1(P) \leftarrow {}^3T_1(F)$ transition shows some detail through either spin-orbit coupling or low-symmetry components, or both, removing the degeneracy of the excited level.

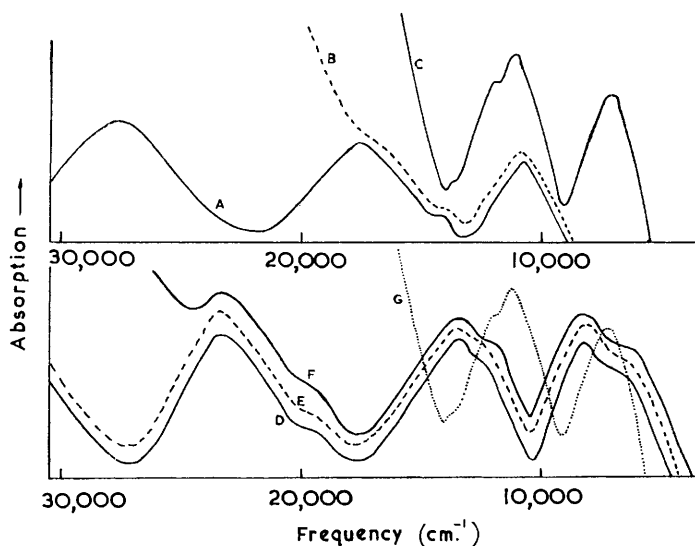


FIG. 4. The reflectance spectra of some solid nickel(II) complexes. A, $\text{Ni}(\text{MeCN})_6(\text{BF}_4)_2$; B, $\text{Ni}(\text{MeCN})_6(\text{Br}_3)_2$; C, $(\text{Et}_4\text{N})_2[\text{NiI}_4]$; D, $\text{NiCl}_2 \cdot 4\text{MeCN}$; E, $\text{NiCl}_2 \cdot 2\text{MeCN}$; F, $\text{NiBr}_2 \cdot 2\text{MeCN}$; G, $\text{NiI}_2 \cdot 3\text{Me}_3\text{CN}$.

Considering the high moments of the $[\text{NiCl}_4^{2-}]$ and $[\text{NiBr}_2^{2-}]$ ions (3.89 and 3.79 B.M.),²³ the moment of $[\text{NiI}_4^{2-}]$ is very low. The root-mean-square of the moments of $(\text{Ph}_3\text{MeAs})_2[\text{NiI}_4]$ and $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ agrees well with the value found for $\text{NiI}_2 \cdot 3\text{MeCN}$ (Table 2), supporting the formulation $[\text{Ni}(\text{MeCN})_6][\text{NiI}_4]$. Nyholm and Gill²³ favour the theory that the moment of $[\text{NiI}_4^{2-}]$ is reduced by mixing of the excited ${}^3A_2(F)$ with the ${}^3T_1(F)$ ground state, while Cotton *et al.*²² suggest that distortion of $[\text{NiI}_4^{2-}]$ from T_d symmetry is responsible for splitting the ground state and quenching some of the orbital angular momentum. The latter explanation seems more reasonable because as Cotton²² points out, there is little difference between the calculated values of Δ for $[\text{NiCl}_4^{2-}]$, $[\text{NiBr}_4^{2-}]$, and $[\text{NiI}_4^{2-}]$ (3580, 3380, and 3350 cm^{-1} , respectively) as would be needed to account for the radical differences between the magnetic moments.

Although $\text{NiI}_2 \cdot 3\text{MeCN}$ crystallises from methyl cyanide solution, solvolysis and decomposition occur when small amounts are redissolved for conductivity measurements and no meaningful results were obtained. These observations agree with those of other writers on the properties of the $[\text{NiI}_4^{2-}]$ ion in methyl cyanide solution.²³

Nickel chloride and bromide form pale yellow-green octahedral complexes, although, in the preparation of $\text{NiBr}_2 \cdot 2\text{MeCN}$, traces of bright blue unstable crystals were found; these are thought to be $\text{NiBr}_2 \cdot 3\text{MeCN}$, formulated in a similar way to the iodide. That some $(\text{NiBr}_4)^{2-}$ ions are present in this solution is shown by its spectra which is dominated by the much more

²² Cotton, Faut, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

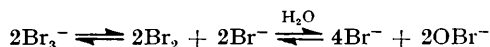
²³ Nyholm and Gill, *J.*, 1959, 3999.

intense peaks due to the tetrahedrally co-ordinated nickel(II) ion. Kern,²⁴ using a slightly different technique, prepared a blue $\text{NiCl}_2 \cdot 3 \cdot 5\text{MeCN}$ although he made no comment regarding its structure; we find its spectrum to be consistent with octahedral nickel(II). Thus, in the complexes of manganese, cobalt, and nickel, $\text{MX}_2 \cdot 3\text{MeCN}$, only the iodides contain $[\text{MI}_4^{2-}]$ ions. This is probably because the iodide ion, relative to the chloride and bromide, has much more covalency associated with its bonding to metal ions by virtue of its greater polarisability.

$\text{NiCl}_2 \cdot 2\text{MeCN}$, $\text{NiCl}_2 \cdot 4\text{MeCN}$, and $\text{NiBr}_2 \cdot 2\text{MeCN}$ have almost identical reflectance spectra (Fig. 4); the second compound is extremely unstable, decomposing almost immediately with loss of methyl cyanide. If the nickel was co-ordinated with four methyl cyanide molecules and two halide ions then there would be an appreciable shift of the spectrum determined by the law of average environment²⁵ and the relative positions of chloride and methyl cyanide in the spectrochemical series. The absence of such a shift suggests that the two additional methyl cyanide molecules are not co-ordinated; and because of its low stability, infrared evidence was inconclusive. The complex is therefore best formulated as $[\text{NiCl}_2 \cdot 2\text{MeCN}] \cdot 2\text{MeCN}$. The near infrared transition, ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}$, is split (Fig. 4) in each of the complexes, and this has only been observed in few cases, such as $\text{NiCl}_2 \cdot 4\text{Py}$ ²⁶ and $\text{NiL}_2(\text{NCS})_2$, where $\text{L} = \text{Et}_2\text{N} \cdot [\text{CH}_2]_2 \cdot \text{NH}_2$.²⁷ The splitting is due to low-symmetry (D_{4h}) perturbations in the octahedra of non-equivalent ligands which split the ${}^3T_{2g}$ into ${}^3B_{2g}$ and 3E_g . The apparent splitting (Fig. 4) of the visible transition ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$, has been discussed by Jørgensen,²⁸ who pointed out that, for complexes with Δ values of 8000 cm^{-1} ($\text{NiCl}_2 \cdot 2\text{MeCN}$ and $\text{NiBr}_2 \cdot 2\text{MeCN}$) the ${}^3T_{1g}(F)$ and ${}^1E_g(D)$ levels are close enough to enable spin-orbit coupling to mix them, so that the transition to the latter gains considerable intensity. However, for Δ values of $10,000 \text{ cm}^{-1}$ ($[\text{Ni}(\text{NH}_3)_6^{2+}]$, $[\text{Ni}(\text{MeCN})_6^{2+}]$) the triplet transition appears as a strong clean band, with the singlet a very weak absorption almost on the base line. At higher energy, another weak singlet is observed followed by the strong ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition.

The magnetic moments of $\text{NiCl}_2 \cdot 2\text{MeCN}$ and $\text{NiBr}_2 \cdot 2\text{MeCN}$ (Table 2) are rather high for octahedral nickel, in which, due to the mixing of orbital angular momentum into the ground state, the observed moments are larger than the "spin-only" magnetic moment. However, spectral evidence indicates that these compounds are distorted from O_h symmetry so that mixing in of orbital angular momentum should be reduced through splitting of the triplet levels, which makes it even more surprising that our observed magnetic moments lie above those normally observed for regular octahedral nickel complexes. However, the reflectance spectrum of $\text{NiCl}_2 \cdot 2\text{Py}$ also shows tetragonal distortion and this complex also has a relatively high magnetic moment of $3 \cdot 37 \text{ B.M.}$ ²⁹ The nickel methyl cyanide complexes are considered to have essentially octahedral structures similar to the manganese complexes.

The reflectance spectrum of the stable brown crystals, represented in Table 1 as $\text{NiBr}_2 \cdot 6\text{L} \cdot 2\text{Br}_2$ is shown in Fig. 4 and is identical with that of $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$ until charge-transfer absorptions occur at $18,000 \text{ cm}^{-1}$ and obscure the remaining $d-d$ bands. The spectrum is strong evidence for $[\text{Ni}(\text{MeCN})_6^{2+}]$ ions, and two possibilities are considered for the structure: (1) $[\text{Ni}(\text{MeCN})_6^{2+}](\text{Br}^-)_2 \cdot 2\text{Br}_2$ or (2) $[\text{Ni}(\text{MeCN})_6^{2+}](\text{Br}_3^-)_2$. Chemical analysis is consistent with either formulation since the reactions³⁰



occur so that four equivalents of bromine are estimated with thiosulphate-iodide and four bromide ions with silver nitrate. Structure (2) is considered the more likely structure since simple halide ions are much stronger co-ordinating ligands than methyl cyanide and it is unlikely that two free bromide ions would allow six methyl cyanide molecules to occupy all six co-ordination sites. Four is the maximum number of methyl cyanide ligands which have been observed in complexes with simple halide ions, and even these are very unstable (*e.g.*,

²⁴ Kern, *J. Inorg. Nuclear Chem.*, 1963, **25**, 5.

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

²⁶ Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

²⁷ Goodgame and Venanzi, *J.*, 1963, 616.

²⁸ Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362; 1957, **11**, 1223.

²⁹ Gill, Nyholm, Barclay, Christie, and Pauling, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88.

³⁰ Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, 1956, Supplement II, Part I, p. 713.

$\text{NiCl}_2 \cdot 4\text{MeCN}$). Although methyl cyanide is a stronger ligand than water, the dielectric constant (81) is large enough to maintain complete dissociation into Ni^{2+} and Cl^- ions so there is, in effect, no real competition between chloride ions and water for co-ordination sites. Methyl cyanide has a dielectric constant of (37.5), less than half that of water and this is not enough to maintain complete dissociation; thus nickel chloride is virtually insoluble in methyl cyanide. Our complex is therefore best considered as (2), where the tribromide ions are much weaker co-ordinating anions than bromide, comparable with BF_4^- , with a single negative charge spread over a large ion. At 100° under vacuum, it decomposes into bromine and bromide, the latter then displacing methyl cyanide, some of which is lost. Four equivalents of bromine can be collected. Similar, although very unstable complexes have been obtained (Table 1) for manganese and cobalt, but their instability relative to the nickel complex is not understood.

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