468. *The Preparation and Properties of Some Bivalent Transition-metal Tetrafluoroborate–Methyl Cyanide Complexes.*

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Manganese, iron, cobalt, nickel, copper, and zinc react with suspensions of nitrosyl tetrafluoroborate in methyl cyanide or ethyl acetate according to the equation $M + 2NOBF_4 = M(BF_4)_2 + 2NO$, to yield solutions of the bivalent-metal tetrafluoroborates. From these solutions the methyl cyanide complexes have been prepared, and some physical properties for both the solid state and solution are reported. Attempts to prepare the anhydrous metal tetrafluoroborates from these complexes resulted in simultaneous loss of methyl cyanide and decomposition of the tetrafluoroborate anion.

THE reaction between copper and suspensions of nitrosyl perchlorate in methyl cyanide and ethyl acetate[1] under reduced pressure proceeds according to the equation $Cu + 2NOClO_4 = Cu(ClO_4)_2 + 2NO$, yielding solutions of anhydrous copper perchlorate in these solvents. The analogous reaction of nitrosyl tetrafluoroborate has now been examined and shown to yield solutions of anhydrous copper tetrafluoroborate. This reaction has been extended to other metals and solutions of their tetrafluoroborates have been prepared, from which the metal tetrafluoroborate–methyl cyanide complexes have been obtained.

EXPERIMENTAL

Nitrosyl tetrafluoroborate[2] was prepared by the reaction of dinitrogen tetroxide on 70% fluoroboric acid and purified by sublimation at 220°.

Preparation of Compounds.—The reaction of suspensions of nitrosyl tetrafluoroborate in methyl cyanide with manganese, iron, cobalt, nickel, and zinc was carried out as previously described for nitrosyl perchlorate.[1] The solution, after filtration, was evaporated to dryness under a vacuum. The solid powders obtained were dissolved in a minimum quantity of hot

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[1] Hathaway and Underhill, *J.*, 1960, 2705.

[2] Grunther, Balz, Erich, and Mailander, *Z. anorg. Chem.*, 1934, **217**, 161.

methyl cyanide, and hot ethyl acetate was added until the solution became cloudy. On cooling, crystals of the methyl cyanide complex settled and were filtered off and dried under a vacuum.

The reaction of copper with suspensions of nitrosyl tetrafluoroborate in methyl cyanide has been shown to yield a mixture of cuprous and cupric tetrafluoroborate,[3] and therefore to prepare the pure cupric compound a suspension of nitrosyl tetrafluoroborate in ethyl acetate was used. No cuprous tetrafluoroborate is produced under these conditions as the ethyl acetate is not a strong enough ligand to stabilise the cuprous ion in solution. At the end of the reaction the solution was filtered, methyl cyanide was added, and the precipitated methyl cyanide complex filtered off. This was then recrystallised as described above.

No evidence of mixed oxidation states was obtained for any metal other than copper.

Analysis.—Cobalt, copper, manganese, and zinc were determined as previously described.[4] Ferrous iron was determined by titration with potassium permanganate, and nickel gravimetrically as nickel dimethylglyoxime. The tetrafluoroborate ion was determined gravimetrically as the nitron salt or as calcium fluoride,[5] both of which methods may give slightly low results.

Analyses of the *complexes* are tabulated.

	Found (%)		Reqd. (%)			
Complex	Metal	BF_4	Metal	BF_4	Colour	M. p.
$Cu(BF_4)_2,4MeCN$	15·8	43·3	15·8	43·3	Blue	168—170°
$Ni(BF_4)_2,6{\cdot}5MeCN$	12·0	34·4	12·2	36·6	Purple	119—122
$Fe(BF_4)_2,6MeCN$	11·9	37·5	11·8	36·5	Off-white	114—116
$Co(BF_4)_2,6MeCN$	12·3	35·4	12·3	36·3	Orange	127—130
$Mn(BF_4)_2,4MeCN$	13·9	44·3	14·0	44·2	White	110—111
$Zn(BF_4)_2,4MeCN$	16·0	42·8	16·2	43·0	White	57—59

Physical Properties.—Molecular weights, electrical conductivities, differential thermal analyses, thermogravimetric analyses, and infrared spectra (of Nujol mulls) were determined as previously described.[3] Visible spectra were measured on a Unicam S.P. 500 spectrophotometer with 1-cm. silica cells. The magnetic susceptibilities were measured with a Gouy balance at room temperature. *X*-Ray diffraction powder patterns were obtained with a Guinier-type powder camera and samples sealed between two sheets of Sellotape; the samples were mounted in a dry-box.

The colours and m. p.s of the methyl cyanide complexes obtained are tabulated. The m. p.s were difficult to define as the compounds softened over a very wide temperature range; those given are the temperatures at which the crystals completely lost their shape to give a clear liquid. The iron compound gave a dark brown melt containing black particles.

RESULTS AND DISCUSSION

Infrared Spectra.—The main infrared absorption frequencies of the six methyl cyanide complexes examined are tabulated. The spectra of the ferrous, cobaltous, and nickelous complexes are very similar to those of silver[6] and potassium tetrafluoroborate.[7] This suggests that the tetrafluoroborate group is purely ionic in the former compounds. The very weak absorption at 765 cm.$^{-1}$ is assigned to the ν_1 frequency and the broad strong absorption in the region 1030—1125 cm.$^{-1}$ to the ν_3 frequency of the tetrafluoroborate ion.[8] The infrared spectra of cupric, manganous, and zinc tetrafluoroborate–methyl cyanide complexes differ from those reported above in two ways. The ν_1 absorption is stronger and the ν_3 absorption is broader and in the case of the manganous and zinc compounds is split into two peaks. The differences in the spectra of the cupric, manganous, and zinc compounds are similar to those already observed in the corresponding perchlorate compounds,[4] suggesting that the factors responsible for the differences in the perchlorates are present here.

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[3] Hathaway, Holah, and Postlethwaite, *J.*, 1961, 3215.

[4] Hathaway and Underhill, *J.*, 1961, 3091.

[5] Booth and Martin, " Boron Trifluoride and its Derivatives," John Wiley and Sons Inc., New York, 1949, p. 238.

[6] Sharp and Sharpe, *J.*, 1956, 1855.

[7] Cote and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 217.

[8] Greenwood, *J.*, 1959, 3811.

Infrared spectra of transition-metal tetrafluoroborate–methyl cyanide complexes.

Mn	2282	2307	1640vw	1308m	1085—1035sb	973vs	942s	765sh
Fe	2287	2310	1636vw	1305m	1128—1036sb		943m	765sh
Co	2292	2316	1633vw	1305m	1075—1033sb		943m	765sh
Ni	2292	2316	1640vw	1308m	1085—1035sb		945w	765sh
Cu	2300	2322	1650w	1308m	1100—1025sb		958m	770w
Zn	2295	2320	1645w	1310m	1174—1091sb	975vs	950s	765m
$AgBF_4$			1529	1300	1064—1026sb			769vw
KBF_4			1700	1300	1075—1050sb			772

sh = shoulder.

A comparison of the infrared spectra of the methyl cyanide complexes of the metal perchlorates and the metal perchlorate dihydrates[4] showed that the bonding between the perchlorate group and the metal ion in the complexes is very weak. No evidence has yet been obtained supporting covalent bonding of the tetrafluoroborate ion to transition-metal ions since this would imply bivalent fluorine.[9] In the tetrafluoroborate[5] complexes with only four molecules of methyl cyanide per metal ion the metal ion may interact with the outer electrons of one of the fluorine atoms to a sufficient extent to make it slightly different from the other three and thus lower the symmetry of the ion to that of C_{3v}.[4] If this does occur then the absorption at 760 cm.$^{-1}$ in the manganous, cupric, and zinc complexes would be the ν_2 frequency of the tetrafluoroborate group with C_{3v} symmetry. The splitting observed in the manganous and zinc complexes and to a smaller extent in the cupric complex would be the splitting of the ν_3 frequency of the tetrafluoroborate ion into the ν_4 and ν_1 frequencies of the tetrafluoroborate group with C_{3v} symmetry. Both these effects would also be observed if the site symmetry of the tetrafluoroborate ion in the crystal was lower than that of T_d.

Magnetic Moments.—The observed magnetic susceptibilities of the complexes, corrected for diamagnetism by use of Pascal's constants,[10] are listed below, along with the corresponding magnetic moment μ, the spin-only magnetic moment, and the range of magnetic moments which have been found experimentally for spin-free complexes.[11] All the methyl cyanide complexes are paramagnetic, except that of zinc, with magnetic moments corresponding to spin-free complexes. This is consistent with the weak ligand field strength of methyl cyanide which places it between water and glycine in the spectrochemical series.[12] A comparison of the observed magnetic moments with the spin-only values shows reasonable agreement with theory. An orbital contribution[11] is predicted for octahedral iron(II) ($d_\epsilon^4 d_\gamma^2$) and cobalt(II) ($d_\epsilon^5 d_\gamma^2$), and the observed values lie well above the spin-only value. No orbital contribution is predicted[11] for manganese(II) ($d_\epsilon^3 d_\gamma^2$), nickel(II) ($d_\epsilon^6 d_\gamma^2$), or copper(II) ($d_\epsilon^6 d_\gamma^3$), but spin-orbital coupling[11] raises the observed moment for nickel and copper slightly above the spin-only value.

Magnetic data for $M^{II}(MeCN)_x(BF_4)_2$ complexes.

	$10^6\chi_M$	$\mu_{eff.}$ (B.M.)	Exp. μ (B.M.)	Spin-only μ (B.M.)
$Mn^{II}(MeCN)_4$	14,600	5·90	5·65—6·10	5·92
$Fe^{II}(MeCN)_6$	12,180	5·42	5·10—5·70	4·90
$Co^{II}(MeCN)_6$	11,070	5·18	4·30—5·20	3·88
$Ni(MeCN)_{6\cdot5}$	4270	3·22	2·80—3·50	2·83
$Cu(MeCN)_4$	1620	1·86	1·70—2·20	1·73
$Zn(MeCN)_4$	—	Diamagnetic	—	—

These magnetic moments give only limited information on the stereochemistry of these

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[9] Sharpe, " Advances in Fluorine Chemistry," Stacey, Tatlow, and Sharpe, Butterworths Scientific Publns., 1960, p. 68.

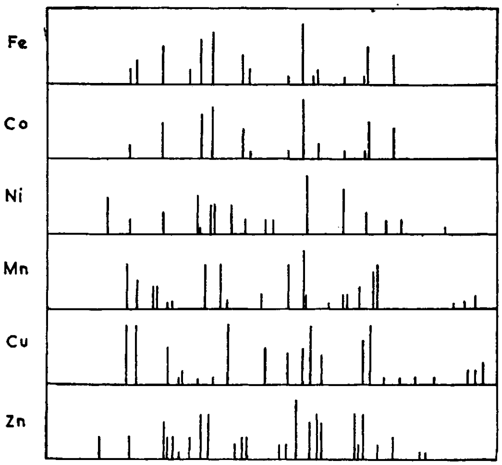
[10] Selwood, " Magnetochemistry," Interscience Publ. Inc., New York, 1956.

[11] Figgis and Lewis, " Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 400.

[12] Jörgensen, " Absorption Spectra of Complexes of Heavy Metals," Technical Report to the U.S. Army, September, 1958.

complexes. Figgis[13] has shown that tetrahedral copper(II) should have a relatively large orbital contribution to its magnetic moment, giving a total moment ∼2·2 B.M. But as a Jahn–Teller distortion[14] may be expected, regular tetrahedral copper(II) is unlikely to exist. This distortion occurs in Cs_2CuCl_4[15] and lowers the magnetic moment from the expected 2·2 to 1·93 B.M.[16] For this reason a magnetic moment of 1·86 B.M. for a complex $Cu(MeCN)_4(BF_4)_2$ is not inconsistent with a distorted tetrahedral configuration for the copper(II) ion, but in view of the spectral properties of this complex (see below) a square coplanar structure is more likely. A magnetic moment of 5·90 B.M. for the manganese complex does not allow a distinction to be drawn between a square coplanar and a tetrahedral structure.

X-*Ray Powder Diffraction Patterns.*—The main lines of the X-ray diffraction powder patterns of the methyl cyanide complexes are represented schematically in the Figure.



X-Ray powder diffraction patterns of metal tetrafluoroborate–methyl cyanide complexes, $M^{II}(MeCN)_x(BF_4)_2$.

These show that only the iron and cobalt complexes are isomorphous and as the cobalt compound is octahedral in solution (see below) it seems likely that the iron complex also involves octahedral co-ordination. Rather unexpectedly the nickel complex gives a radically different pattern, and, since it too has an octahedral co-ordination in solution, this difference confirms the analysis which indicates 6·5 moles of methyl cyanide per nickel atom. The extra half molecule of methyl cyanide is probably only bound in the crystal lattice but this is sufficient to destroy the isomorphism with the cobalt and iron complexes.

The three tetrakis(methyl cyanide) complexes (manganese, copper, and zinc) exhibit different powder patterns and do not give any direct help in deciding whether these complexes involve tetrahedral or square coplanar co-ordination. But if the copper compound is assumed to be square coplanar with respect to methyl cyanide, this does not rule out a similar four-square-coplanar structure for the manganese complex. In both of these complexes an irregular octahedral structure probably exists in the solid state, with the tetrafluoroborate ions occupying the co-ordinate positions above and below the central metal ion. But owing to the Jahn–Teller[14] effect the copper complex will give a much longer bond in this z-direction than manganese will and hence destroy the isomorphism of these two complexes. As the powder pattern of the zinc complex is different from that of the manganese and copper complexes, and as four co-ordinate zinc is commonly tetrahedral, this is the most likely configuration for the zinc complex.

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[13] Figgis, *Nature*, 1958, **182**, 1568.

[14] Orgel and Dunitz, *Nature*, 1957, **179**, 462.

[15] Helmholz and Kruh, *J. Amer. Chem. Soc.*, 1952, **74**, 1176.

[16] Meyers (Massachusetts Institute of Technology), unpublished observation.

Thermogravimetric and Differential Thermal Analysis—Thermogravimetric analysis of all six complexes showed that loss of methyl cyanide and decomposition of the tetrafluoroborate anion occurs simultaneously and that the anhydrous metal tetrafluoroborate cannot be obtained by controlled decomposition. In general the corresponding impure metal fluoride was obtained. Differential thermal analysis showed that endothermic decomposition occurs between 170—240°, which agrees with the temperature at which the most rapid loss of weight was recorded on the thermobalance.

Apparent Molecular Weights and Molar Conductivities.—The results (see Table) indicate that these complexes are more than 50% dissociated in this solvent and in view of the much lower conductivity of anhydrous copper nitrate (20 ohm^{-1} cm.$^{-2}$ in 0·1M-solution), which is known to be monomeric in this solvent,[17] it is suggested that the association involves ion association and not co-ordination of the tetrafluoroborate ions to the metal ions. Consequently in these solutions the cations may be considered as completely solvated by methyl cyanide, probably by octahedral co-ordination in all cases.

Apparent molecular weights and molar conductivities (ohm^{-1} cm.$^{-2}$) of metal tetrafluoroborate complexes in 0·1M-solutions in methyl cyanide.

	Mn	Fe	Co	Ni	Cu	Zn
App. *M*	111	103	113	123	153	120
M	229	230	233	233	237	239
Molar condy.	143	152	151	152	137	145

Visible Absorption Spectra.—Solutions of manganese, iron, and zinc tetrafluoroborate in methyl cyanide are colourless, but those of cobalt, nickel, and copper are coloured; details are:

	Cobalt	Nickel				Copper
$\lambda_{\text{max.}}$ (cm.$^{-1}$)	20,400	27,560	17,090	13,940	10,530	13,320
$\varepsilon_{\text{max.}}$ (l. mole^{-1} cm.$^{-1}$)	15·4	51·0	34·3	8·7	38·8	21·8

The cobalt complex has a single absorption at 20,400 cm.$^{-1}$, which is consistent with an octahedral co-ordination [18] [*e.g.*, $Co(NH_3)_6^{2+}$ absorbs at 20,000 cm.$^{-1}$]. A tetrahedrally co-ordinated cobalt(II) ion [19] has two absorptions in the visible region both with much higher extinction coefficients ($\varepsilon > 500$). The nickel complex has four absorptions in the visible region, consistent with an octahedral co-ordination [20] [*e.g.*, $Ni(NH_3)_6^{2+}$ absorbs at 28,200, 17,500, 13,150, and 10,750 cm.$^{-1}$]. The copper complex has a single very broad absorption which probably involves either two [21] or three [22] overlapping absorptions and is consistent with a distorted octahedral co-ordination.[20] Tetrahedral co-ordination of copper(II) would require no absorption in the visible region.[23]

The authors are indebted to Dr. G. W. Gray for the infrared measurements, to Mr. G. A. Steigmann for the powder photographs, to Professor C. C. Addision for the use of his magneto balance, to the Chemical Society for a grant for apparatus, and to the Department of Scientific and Industrial Research for maintenance grants (to D. G. H. and A. E. U.).

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[*Received, September* 18*th*, 1961.]

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[17] Addison, Hathaway, Logan, and Walker, *J.*, 1960, 4308.
[18] Orgel, *J. Chem. Phys.*, 1955, **23**, 1005.
[19] Holm and Cotton, *J. Chem. Phys.*, 1959, **31**, 788.
[20] Manch and Fernelius, *J. Chem. Educ.*, 1961, **38**, 192.
[21] Graddon, *J. Inorg. Nucl. Chem.*, 1960, **14**, 161.
[22] Belford, Calvin, and Belford, *J. Chem. Phys.*, 1957, **26**, 1165.
[23] Bannister and Cotton, *J.*, 1960, 1878.