The Properties of the Hexanitro Complexes of Divalent Iron, Cobalt, Nickel, and Copper

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The X-ray powder photographs, magnetic susceptibilities, infrared spectra, electronic spectra (as reflectance), and electron-spin resonance spectra of nine hexanitro complexes of divalent iron, cobalt, nickel, and copper are reported. They are of the form $K_2M'[M''(NO_2)_6]$ where M'' is a divalent transition metal ion and M' is a divalent cation (lead or barium, and, in the case of the copper complex, calcium). All the complexes were confirmed as having face-centered cubic crystal structures except for the barium–copper and the calcium–copper complexes, which were shown to be weakly tetragonal. The unit cell dimension a of the cubic lead complexes shows a systematic increase from iron to copper corresponding to an increase in the metal to nitrogen distance in this sequence, consistent with the increasing repulsion experienced by the ligands as electrons are added to the e_g orbitals. The electronic reflectance spectra of the iron and nickel complexes are consistent with a regular octahedral coordination and a crystal field splitting of 13,590 cm^{-1} is indicated for the nickel complex, the highest value yet reported for a spin-free octahedral nickel(II) complex. The electronic spectra of the cobalt and copper complexes closely resemble one another and are only consistent with a tetragonal environment for the transition metal ions. The observation of an isotropic electron spin resonance spectrum for the lead–copper, the lead–cobalt, and the barium–cobalt complexes, but an anisotropic spectrum for the barium–copper and calcium–copper complexes, suggests that the former complexes may be undergoing a dynamic Jahn–Teller distortion.

Introduction

A wide range of hexanitro complexes of the first-row transition metal ions are known,[1-5] many of which have been shown to have face-centered cubic crystal structures;[4,6-8] those of the divalent iron and cobalt ions have been shown to involve spin-paired electron configurations.[9-11] In view of the novelty of a cubic structure for the spin-paired cobalt(II) ion and for the copper(II) ion as six-coordinate complexes, the lead and barium series of the complexes of the divalent iron, cobalt, nickel, and copper ions have been reexamined both crystallographically and using the current techniques of inorganic chemistry; the results have been interpreted using ligand field theory.

Experimental Section

Preparation.—All of the complexes examined have been previously reported, but for a number of the complexes the analyses reported were not very good[10] and slight modifications of the preparative details were found necessary to obtain pure products; brief details of these modifications are reported. Attempts to prepare the manganese(II) and zinc(II) complexes of these series were unsuccessful.

Method A.—An aqueous solution of the divalent transition metal nitrite (0.05 mole) in 80 ml of water was added to a mixture of potassium nitrite (0.10 mole) and barium nitrite monohydrate (0.05 mole) (A_1) or lead acetate (0.05 mole) (A_2) or calcium nitrite (0.05 mole) (A_3), where appropriate, in 80 ml of water. In general, the complexes were immediately precipitated as fine pow-

ders, the exceptions being the copper complexes. The lead–copper complex crystallized out immediately, but the barium–copper and calcium–copper complexes required the addition of ethanol. The preparation of the copper complexes required the addition of a few drops of glacial acetic acid to prevent the formation of basic hydrolysis products.

Method B.—A mixture of the transition metal nitrate (0.05 mole) and barium nitrite monohydrate (0.05 mole) (B_1) or lead nitrite (0.05 mole) (B_2) in 80 ml of water was added to an excess of an aqueous solution of potassium nitrite (2 moles) in 80 ml of water. The preparation of the ferrous complexes required the addition of sodium acetate (0.125 mole) to act as a buffer, as otherwise very rapid decomposition of the solution occurred, with evolution of nitric oxide.

Analysis.—In all cases, the samples were dissolved in 1 ml of concentrated nitric acid and evaporated to dryness to oxidize nitrite ion to nitric oxide. Lead and barium were determined as the respective sulfates after removal of nitric acid by evaporation with concentrated sulfuric acid. The transition metals were determined by normal gravimetric methods[12] after removal of lead, where appropriate, and of barium, in the case of the iron complexes.

The infrared spectra were recorded as KBr disks (after checking that no exchange occurs with the potassium bromide) on a Unicam S.P. 100 spectrophotometer, and the electronic spectra (as reflectance spectra) on a Beckman D.K. 2A. recording spectrophotometer fitted with a standard reflectance attachment in the range 4000–40,000 cm^{-1}. The room-temperature electron spin resonance spectra were recorded on a Hilger and Watt microspin spectrometer internally calibrated with diphenyl hydrazyl picrate, and the low-temperature spectra on a Varian electron spin resonance spectrophotometer. The X-ray powder photographs were recorded on a Guinier type focusing camera, internally calibrated with aluminum powder. The room-temperature magnetic data were obtained using a Gouy-type balance.

Results

Crystallographic Data.—The unit cell dimensions, a, for a series of cubic hexanitrometallate(II) complexes have been previously reported;[10] these have been re-

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(1) C. Przibylla, *Z. Anorg. Chem.*, **15**, 419 (1897).
(2) M. van Lessen, *Rec. Trav. Chim.*, **10**, 13 (1891).
(3) F. Ephraim, *Helv. Chim. Acta*, **6**, 920 (1923).
(4) A. Ferrari and C. Colla, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis., Mat. Nat.*, **11**, 755 (1930); **14**, 435, 511 (1931).
(5) A. Ferrari and C. Colla, *Gazz. Chim. Ital.*, **65**, 168, 809 (1935).
(6) A. Ferrari and R. Curti, *ibid.*, **63**, 499 (1933).
(7) M. van Driel and H. J. Verweel, *Z. Krist.*, **A95**, 308 (1936).
(8) J. E. MacKenzie and R. L. Smith, *Rec. Trav. Chim.*, **57**, 1211 (1938).
(9) P. Ray and H. Sahu, *J. Indian Chem. Soc.*, **23**, 161 (1946).
(10) L. Cambi and A. Ferrari, *Gazz. Chim. Ital.*, **81**, 1162 (1951).
(11) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

(12) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," 2nd ed, Longmans, Green and Co., London, 1951.

| M' | M'' | Analysis, % | | | | Method of prepn | Color | Unit cell, A | | μ_{eff} |
| | | Found | | Calcd | | | | | | |
		M'	M''	M'	M''			a (ref 10)	a	
Pb	Fe	33.4	9.03	33.6	9.04	B$_2$	Orange	10.31	10.36	0.858
Ba	Fe	24.8	10.01	25.1	10.20	B$_1$	Orange	10.43	10.54	0.916
Pb	Co	33.6	9.38	33.4	9.50	A$_2$	Brown	10.40	10.51	1.82
Ba	Co	24.9	10.68	25.0	10.70	A$_1$	Green	10.45	10.67	1.88
Pb	Ni	33.7	9.29	33.4	9.47	A$_2$	Buff	10.55	10.60	2.99
Ba	Ni	25.1	10.32	25.0	10.70	A$_1$	Buff	10.67	10.81	3.12
Pb	Cu	33.0	10.19	33.2	10.17	A$_2$	Brown	10.65	10.70	1.94
Ba	Cu	24.8	11.28	24.0	11.43	A$_1$	Green		...^{a}	1.96
Ca	Cu	8.54	13.81	8.75	13.88	A$_3$	Green		...^{a}	1.83^9

^{a} Tetragonal c/a ratio, Ba = 1.046, Ca = 1.040.

determined and the results, giving slightly larger values of the cubic cell dimensions, are shown in Table I. The barium– and calcium–copper complexes are shown to be weakly tetragonal. From the systematic absences in the (h,k,l) values of the cubic complexes, a face-centered cubic structure was confirmed; from the stoichiometry and the presence of four molecules per unit cell, the lead or barium ions are placed at the corners and centers of the faces of the unit cell, with the [M(NO$_2$)$_6$]$^{4-}$ anions in special positions at the center of the unit cell and at the midpoints of all the edges. The potassium ions then occupy positions on all the diagonals at a distance of one-quarter of the length of the diagonal from each corner.

In the face-centered cubic unit cell, the space group restricts the possible symmetries of the complex anion to O, O$_h$, T, T$_h$, or T$_d$[7]. Of these, O and O$_h$ are restricted to coordination in which the nitrite oxygens are placed at the midpoints of the edges of the octahedron, a situation which would give unusually long N–O distances[7] and so is not considered a likely symmetry. Coordination though nitrite nitrogen is most likely and, if free rotation of the nitrite groups about the nitrogen–metal ion bond occurs, the symmetry would be O. If, however, the nitrite oxygens have fixed orientations within the hexanitrometallate group, either T$_h$ or T$_d$ symmetry can arise (Figure 1), of which the former is preferred on the grounds that it minimizes the interactions between the terminal nitrite oxygen atoms.

The crystallographic data for the barium–copper and calcium–copper complexes have not been previously reported. These have been shown to have tetragonal unit cells with c/a ratios of 1.046 and 1.040, respectively, suggesting only a small distortion from cubic symmetry.

In the cubic complexes, the unit cell dimensions, a, increase systematically from iron to copper in both the lead and barium series (as far as they go) with the a values for the barium series being approximately 0.2 A larger; this is consistent with the greater ionic radius of the barium(II) ion, 1.35 A on the Pauling scale, compared with 1.21 A for the lead(II) ion. Why both the lead–cobalt and barium–cobalt, but only the lead–copper complexes are cubic is not understood, but as both the barium–copper and calcium–copper complexes are tetragonal with $c/a > 1$ it would suggest that there must be something special about the lead ion
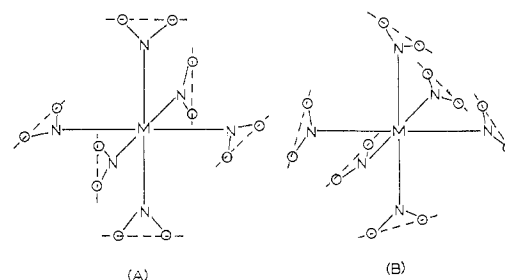

Figure 1.—The possible configurations of the [M(NO$_2$)$_6$]$^{4-}$ anion with fixed orientations of the NO$_2$$^-$ groups. (A) T$_h$ symmetry; the planes of the NO$_2$$^-$ groups *trans* to each other are coplanar and parallel to the cartesian directions. (B) T$_d$ symmetry; the planes of the NO$_2$$^-$ groups *trans* to each other are at 90° and these planes are at 45° to the cartesian directions.

which stabilizes the cubic structures. This is especially so as the ionic radius of the lead(II) ion (1.21 A) is intermediate between that of the barium(II) (1.35 A) and the calcium(II) ions (0.99 A). The unique position of the lead–copper complex in having a cubic unit cell at room temperature is emphasized by the loss of this cubic structure between room temperature and −38°. Unfortunately, the quality of the low-temperature powder photographs was not good enough to allow a complete interpretation, except to say that it differed significantly from the tetragonal powder patterns of the barium–copper and calcium–copper complexes. But this does not rule out the possibility that the low-temperature form of the lead–copper complex is tetragonal.

The unit cell dimension, a, increases by approximately 0.2 A from the lead to the barium complex of a given metal ion; this would suggest that, if a cubic barium–copper complex did exist, it would have an a value of approximately 10.9 A. In practice, this complex is tetragonal with $a = 10.7$ A and $c = 11.25$ A, which indicates that not only is there an elongation of the copper environment in the c direction (z axis) but that this is accompanied by a contraction in the x and y directions compared with a cubic environment. This suggests a pictorial approach to the process of distortion, when the movement of the ligands outward in the z direction is accompanied by a simultaneous contraction in the x and y directions. This effect has been observed in the difluorides of the first-row transi-

TABLE II

INFRARED SPECTRA (CM^{-1}) OF THE HEXANITRO COMPLEXES $K_2M'M''(NO_2)$

M'	M''	ν_{asym}			ν_{sym}			δ	
Pb	Fe	1637 vw	1565 vw		1320 vs	1300 vs	1190 m, sp	830 s, sp	
Ba	Fe	1630 vw			1332 vs		1184 m, sp	820 s, sp	
Pb	Co	1650 vw		1410 sh	1322 s	1296 sh	1230 sh	830 s	
Ba	Co	1650 vw		1400 s	1330 s	1292 sh	1250 sh	826 s	
Pb	Ni	1650 vw	1580 vw	1428 m, sh	1322 vs		1244 m, sh	856 w	822 s, sp
Ba	Ni	1640 vw		1405 m, sh	1348 s	1341 vs		836 w	810 m, sp
Pb	Cu				1340 s	1280 s		842 s	
Ba	Cu	1630 vw		1420 m, sh	1332 s	1260 s		816 s	800 s
Ca	Cu				1340 s	1294 s		832 s	820 m, sh

M'	M''	δ_w	M–N		δ_{NO_2}	
Pb	Fe	645 w	406 m			270 m
Ba	Fe	644, 607 w	408 m			292 m
Pb	Co	629	412 m	381 s	320 s	260 m
Ba	Co		418 m	384 w	326 w	293 s
Pb	Ni		440 w		293 s	288 s
Ba	Ni		435 w		296 s	285 s
Pb	Cu		441 w		320 s	288 s
Ba	Cu	556 vw	447 w		315 s	288 s
Ca	Cu	471 m	451 w	351 s	312 s, sh	291 s

tion metal ions.[13] If a copper–nitrogen distance of 2.15 A[7] is assumed for a regular octahedral environment of the copper(II) ion, the differences of the tetragonal *a* and *c* lengths from 10.9 A give an approximate measure of the tetragonal distortion of the environment of the copper(II) ion in the barium–copper complex. The contraction in the *xy* plane is 0.2 A distributed between two copper–nitrogen bonds, giving a final copper–nitrogen distance of 2.05 A. The elongation in the *z* direction is 0.35 A, or 0.18 A per bond, giving an axial bond length of 2.33 A. If the difference between these two bond lengths is taken as a measure of the total distortion, the value of 0.28 A suggests that the copper ion environment in the barium–copper complex is subjected to a relatively small distortion, the normal static distortion being 0.6 A.[14] The *a* values of the calcium complexes have not been measured, but the *c/a* ratio of the calcium–copper complex is smaller than that of the barium–copper complex, implying that the distortion may be even smaller.

Magnetic Data.—The room-temperature magnetic moments (μ_{eff}) of the hexanitrometallate(II) complexes as determined in the present work are given in Table I; they are in reasonable agreement with the data of Cambi and Ferrari[10] and Figgis and Nyholm.[11] The magnetic moments show that these hexanitrometallates(II) of iron, cobalt, nickel, and copper have zero, one, two, and one unpaired electrons, respectively. These results suggest that the transition metal ions in these cubic complexes are in octahedral environments with ground state electron configurations and terms $t_{2g}^6 e_g^0(^1A_{1g})$, $t_{2g}^6 e_g^1(^2E_g)$, $t_{2g}^6 e_g^2(^3A_{2g})$, and $t_{2g}^6 e_g^3(^2E_g)$ for the iron(II), cobalt(II), nickel(II), and copper(II) ions, respectively. This indicates that the crystal field due to six nitrite ions is sufficiently strong to produce spin pairing in the iron(II) (d^6) and cobalt(II) (d^7) ions. This is consistent with the general readiness of iron(II) to assume a spin-paired configuration and con-

trasts with the general tendency of cobalt(II) to form spin-free complexes (even tris-1,10-phenanthroline-cobalt(II) is spin-free,[11] while the corresponding iron(II) complex is spin-paired[15]) and suggests that the nitrite ion produces a stronger crystal field than 1,10-phenanthroline and hence is placed higher in the spectrochemical series (see Electronic Spectra).

The iron(II) complexes are essentially diamagnetic, but the presence of a small amount of temperature-independent paramagnetism of approximately 200 × 10^{-6} cgsu/mole accounts for the nonzero values of μ_{eff} observed. The μ_{eff} values of the cobalt(II), nickel(II), and copper(II) complexes are all slightly higher than the spin-only values, but these results, along with their temperature variation, will be discussed elsewhere.

Infrared Spectra.—The results are given in Table II, from 1700 to 250 cm^{-1}. The infrared spectrum of an ionic nitrite[16] involves the NO_2 antisymmetric stretch at approximately 1300 cm^{-1}, the NO_2 symmetric stretch at 1200 cm^{-1}, the NO_2 bending mode at 825 cm^{-1}, the NO_2 wagging mode at 600–650 cm^{-1}, and the NO_2 rocking at 250–350 cm^{-1}. In some cases, it is difficult to separate out the asymmetric and symmetric NO_2 stretching modes as these occur close together and overlap. When the nitrite ion is involved in coordination to a transition metal ion through its nitrogen atom, its C_{2v} symmetry is maintained and the number of infrared vibrations is unchanged, but there may be small changes in the frequencies. Consequently, the infrared spectra do not allow a clear distinction to be drawn between the presence of an ionic or coordinated nitro group. The infrared spectra of the hexanitrometallate(II) complexes are consistent with the presence of the hexanitrometallate(II) anion, but differences in detail occur between the different transition metal ions. All the complexes give a strong peak at approximately 1330 cm^{-1} which is sometimes split.

(13) C. Billy and H. M. Haendler, *J. Am. Chem. Soc.*, **79**, 1049 (1957).
(14) J. D. Dunitz and L. E. Orgel, *Nature*, **179**, 462 (1957).
(15) A. Kiss and J. Csaszar, *Acta Chim. Hung. Tomus.*, **38**, 406 (1963).
(16) K. Nakamoto, "Infrared-red Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 151–155.

TABLE III

THE ELECTRONIC (REFLECTANCE[a]) SPECTRA (CM^{-1} × 10^{-3}) OF THE COMPLEXES K$_2$M'M''(NO$_2$)$_6$

M'	M''												
Pb	Fe					20.83	(1.8)	25.51	(1.9)	30.30 sh	(1.6)	38.77	(1.6)
Ba	Fe					22.22 sh	(1.65)	26.64	(1.8)	31.65	(1.5)	37.04	(1.45)
Pb	Co	7.69	(0.6)	15.4	(1.9)[b]	18.7	(1.9)			32.47	(1.6)	40.49	(1.5)
Ba	Co	7.14	(0.4)	15.92	(1.3)			23.53	(1.7)	30.86	(1.8)	40.32	(1.6)
Pb	Ni	10.87 sh	(0.2)	13.59	(0.6)	20.58	(1.3)	26.32	(1.8)	32.36	(1.8)	38.17	(1.6)
Ba	Ni	10.99 sh	(0.2)	13.59	(0.6)	20.66	(1.3)	29.07	(2.0)	30.30	(1.9)	40.49	(1.7)
Pb	Cu	7.02	(0.6)	16.6 sh	(1.3)	19.8 sh	(1.5)	26.5	(1.7)			39.2	(1.5)
Ba	Cu	7.88	(0.7)	16.53	(1.3)	24.8 sh	(1.6)	28.9	(1.9)			39.7	(1.5)
Ca	Cu	7.88	(0.7)	16.53	(1.5)	21.85	(1.5)	29.2	(1.5)			36.8 sh	(1.2)

[a] The intensity scale of reflectance spectra is arbitrary, but in order to give an idea of the relative intensity of the peaks a scale of 0–2 is quoted in parentheses. [b] Very broad on the high-frequency side.

In addition, the iron complexes give a medium sharp peak at 1190 cm^{-1}. The cobalt and copper complexes both give strong peaks at 1300 cm^{-1}, but these are at the maxima of very broad absorptions, in contrast to the iron and nickel complexes which give very strong, sharp peaks in this region.

The NO$_2$ bending mode appears as a single, sharp peak in the spectra of cubic salts of the hexanitrocobalt-(III) anion,[17] but is split in the case of the noncubic sodium salt. Consistent with this, the spectra of all the cubic hexanitrometallate(II) complexes of the present work show a single, sharp peak at 830–820 cm^{-1}, but there is clear evidence of splitting in the cases of the tetragonal barium– and calcium–copper complexes. The presence of a weak absorption at 856 and 836 cm^{-1} in the spectra of the lead– and barium–nickel complexes, respectively, is not understood, but a band in this region also occurs in a number of other complexes containing the hexanitronickel(II) anion.[18]

In the cesium iodide region, the NO$_2$ wagging mode is not observed for all the complexes, but the NO$_2$ rocking mode appears strongly in every case, appearing to be split in all spectra except those of the iron complexes. By comparison with the spectra of the cubic hexanitrocobalt(III) complexes,[17] the bands at 450–400 cm^{-1} are assigned to the metal–nitro asymmetric stretching mode and show a small increase in frequency with increasing atomic weight of the central metal ion. The appearance of the nitrogen–metal bands in this region for these nitro complexes agrees with the suggested assignment of the metal–nitrogen asymmetric stretching mode of the divalent hexaammine complexes to the region 320–270 cm^{-1},[19] the partial double bond character of the metal–nitrite bond raising the frequency above that of the corresponding vibration of the hexaammine which must involve pure σ bonds.

A comparison of the infrared spectra of the corresponding barium and lead series of hexanitrometallates showed no clear differences, suggesting that there can be little difference in the environment (twelve oxygen atoms) of the barium and lead ions in these complexes.

Electronic Spectra.—As it is the properties of the complexes in the solid state which are being examined in this paper, the electronic spectra were all recorded as reflectance spectra of powdered samples, Table III. Attempts to record the solution spectra were unsuccessful as only the copper complexes are reasonably soluble in water and even these solutions are subject to hydrolysis and deposition of basic material.

The spectra of the nickel complexes show two low-intensity bands before the onset of high-energy bands. The two low-energy bands are assigned to the $^3T_{2g}(F) \leftarrow$ $^3A_{2g}$ and $^3T_{1g}(F) \leftarrow$ $^3A_{2g}$ transitions of the nickel(II) ion in a regular octahedral environment[20] of nitrite nitrogen atoms, the ground state being $^3A_{2g}$, as indicated by the magnetic data. The energy of the lowest frequency band[21] gives the value of $10Dq$ directly as 13,590 cm^{-1}, which is the highest value reported for the nickel(II) ion with a $^3A_{2g}$ ground state in a regular octahedral environment. The values of $10Dq$ for the tris-2,2'-bipyridylnickel(II) and tris-1,10-phenanthrolinenickel(II) ions are 12,650 and 12,700 cm^{-1}, respectively;[22] therefore, the monodentate nitrite ion must lie even higher in the spectrochemical series[23] for the nickel(II) ion than these two bidentate nitrogen ligands.

Jørgensen[24] has reported the solution spectrum of the nickel(II) ion in 10 M sodium nitrite solution; it consists of three d–d bands at 10,100, 16,600, and 22,400 cm^{-1}, as that of the hexanitronickel(II) ion. A calculation based on the law of average environment and using a value of 13,590 cm^{-1} as $10Dq$ for the hexanitronickel(II) ion suggests that the species present in an excess of sodium nitrite is the dinitrotetraaquonickel(II) ion, which is consistent with a strongly tetragonal environment as suggested by Jørgensen.

The energy level diagram[25] for the nickel(II) ion in an octahedral crystal field suggests that for a numerical value of $10Dq$ as high as 13,590 cm^{-1}, the spin-forbidden transition to the ^1E_g state should lie below the first ligand field band while the transition to $^1A_{1g}$ should coincide with the transition to $^3T_{1g}(F)$. The reflectance spectra do show a weak absorption at 10,900 cm^{-1}

(17) I. Nakagawa, T. Shimanouchi, and K. Yamasaki, *Inorg. Chem.*, **3**, 772 (1964).

(18) M. Le Postollec, J. P. Mathieu, and H. Poulet, *J. Chim. Phys.*, **60**, 1319 (1963).

(19) Reference 16, p 146.

(20) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., London, 1962, p 261.

(21) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).

(22) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 297.

(23) Reference 22, p 107.

(24) C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p 84.

(25) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

which is assigned as $^1E_g \leftarrow {}^3A_{2g}$, but no evidence of absorption at about 21,000 cm^{-1} is observed as it is masked by the spin-allowed $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition, which occurs at 20,600 cm^{-1}.

The octahedral nickel(II) ion should give rise to a third d–d transition, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, at approximately 30,000 cm^{-1} which is usually of slightly higher intensity than the first two bands. In both of the nickel(II) spectra reported, an intense band does occur in this region but it is impossible to say whether this is due to the above d–d transition, to a charge-transfer transition, or to a ligand transition[26] which has been shifted from the free nitrite ion frequencies of 50,000 and 29,000 cm^{-1}, by coordination.

The spectra of the iron complexes give no indication of any d–d transitions as these are masked by high-energy bands, but the peaks at 20,830 and 22,200 cm^{-1} for the lead and barium complexes, respectively, are probably of the same nature as similar bands[15] in this region for tris(2,2′-bipyridyl)- and tris(1,10-phenanthroline)iron(II) complexes, which are interpreted as Laporte-allowed electron transfer from the filled $t_{2g}{}^6$ orbitals to a ligand π orbital.

The electronic spectra of the cobalt(II) and copper(II) complexes closely resemble each other, which is understandable as both the d^9 and the spin-paired d^7 configurations have $^2E_g(^2D)$ ground states. The spectrum of the cubic lead–copper complex closely resembles those of the tetragonal barium– and calcium–copper complexes. The spectrum of an ion with an ^2E_g ground state in a regular octahedral environment should consist of a single peak at an energy of the approximate value of $10Dq$ for the octahedral nickel(II) ion, namely 13,600 cm^{-1}, possibly split by, at the most, 1300 cm^{-1} due to spin-orbit coupling.[27] All the cobalt and copper spectra contain two clear bands in this region, a relatively strong absorption at approximately 16,000 cm^{-1} and a less intense band at 7500 cm^{-1}. The spectra of the cubic hexanitro complexes are thus inconsistent with an octahedral arrangement of the nitrite nitrogens and, in view of the similarity to the tetragonal barium–copper spectrum, suggest that all of these spectra should be interpreted as arising from a tetragonal environment for the central ions.

The assignment of the electronic spectra of the cobalt and copper complexes can be considered in two ways, Figure 2. If the environment is considered to have a static tetragonal distortion (which does not arise from the operation of the Jahn–Teller effect[28]), then the splitting of the ^2D term in crystal fields of O$_h$ and D$_{4h}$ symmetry[29] is as shown in Figure 2A. The assignment of the two observed transitions is then as $^2A_{1g} \leftarrow {}^2B_{1g}$ and ^2E_g, $^2B_{2g} \leftarrow {}^2B_{1g}$, for the bands at 7500 and 16,000 cm^{-1}, respectively. It is unusual to observe such a clear separation of these two bands in the spectra of copper(II) complexes, as they usually tend to overlap to produce a single broad asymmetric band. In the
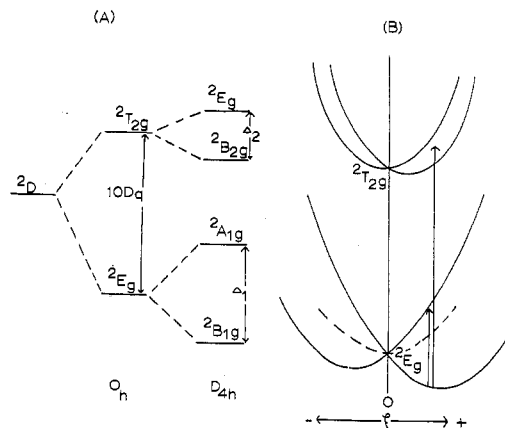
(26) J. W. Sidman, *J. Am. Chem. Soc.*, **79**, 2669 (1957).
(27) Reference 20, p 118.
(28) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937).
(29) Reference 20, p 102.

Figure 2.—(A) The splitting of a ^2D spectroscopic term in crystal fields of O$_h$ and D$_{4h}$ symmetry. (B) The splitting of the degenerate levels of the copper(II) ion in an octahedral field by the action of a nontotally symmetric vibration ξ.

case of the hexanitrometallate complexes it is possible that the occurrence of a relatively small tetragonal distortion combined with a numerically large value of $10Dq$ of approximately 13,600 cm^{-1} results in a clear separation of these two transitions. By assuming that the higher band is a transition from the center of the split $^2T_{2g}$ level and subtracting half the energy of the $^2A_{1g} \leftarrow {}^2B_{1g}$ transition from this, it is possible to obtain an approximate value of $10Dq$ (A). These are as shown in Table IV. A reasonably consistent value of $10Dq$ is obtained, which is slightly lower than that for the hexanitronickel(II) complexes. Using this assignment, all the bands above 17,000 cm^{-1} are considered to be due to either charge-transfer or nitrite n–π^* transitions.[26]

TABLE IV

		Pb–Cu	Ba–Cu	Ca–Cu	Pb–Co	Ba–Co
A	$10Dq$	13,600	12,600	12,600	12,400	12,300
B	$10Dq$	15,200	18,100	16,100	14,000	17,200
	Δ_1	3,200	2,700	5,300	2,400	7,600
	Δ_2	7,020	7,880	7,880	7,850	7,520

In the case of the copper complexes, the bands between 19,000 and 25,000 cm^{-1} are assigned to charge-transfer transitions. As these are only slightly more intense than the bands at 16,500 cm^{-1} and their energies are rather low for charge-transfer bands, an alternative assignment is to treat them as d–d transitions (B). This implies that we can now see all the transitions shown in Figure 2A and involves the assignment of the band at 16,500 cm^{-1} as the $^2B_{2g} \leftarrow {}^2B_{1g}$ transition and the next highest band as the $^2E_g \leftarrow {}^2B_{1g}$ transition. Using this assignment, the calculated values of $10Dq$, Δ_1, and Δ_2 are as shown in Table IV. The calculated values of $10Dq$ using assignment B are much larger than with A and there is more scatter between the values for the different complexes. The two lead complexes give the lowest values of $10Dq$, while the barium–copper and barium–cobalt complexes give surprisingly similar results considering that the former is tetragonal while the latter is cubic in structure. For

these reasons, assignment A is preferred and the low-energy bands of the lead complexes at 19,800 and 18,700 cm^{-1} are considered to be due to charge-transfer bands which may be associated with the presence of the highly reducing lead(II) ions.

The possibility that the low-energy band (≈ 7000 cm^{-1}) is a forbidden internal ligand or metal–ligand transition is not considered very likely as they do not appear in the iron(II) or nickel(II) hexanitrometallate spectra.

The measurement of the reflectance spectra of these complexes at the temperature of liquid air produced no further splitting of the d–d bands, but only effected a shift of approximately 500 cm^{-1} to higher frequencies. It is rather surprising that the band at 16,500 cm^{-1} did not show evidence of splitting; it implies that the splitting of the $^2T_{2g}$ level, scheme A, is very small (less than 2000 cm^{-1}), which is surprising for coordination by six nitrite ions which are able to act as π-bonding (acceptor) as well as σ-bonding (donor) ligands, but may be consistent with the nitro group being only a weak π-bonding ligand intermediate between the π-donating halide ions and the π-accepting cyanide ligands.[30]

The assignment of the electronic spectra of these cobalt(II) and copper(II) complexes has so far only been considered in terms of a statically distorted environment using a purely crystal field model. An alternative approach is to consider the static distortion to arise, at least in part, as a consequence of the Jahn–Teller effect[28,31–33] and to consider the symmetry predominantly in terms of this effect. In this case, it is not possible to separate electronic effects from nuclear displacements and it is necessary to consider the type of potential energy diagram shown in Figure 2B. The effect of nuclear displacement is to split the orbital degeneracy of the ^2E_g and $^2T_{2g}$ terms into two potential surfaces, the separation of which is greater for the ^2E_g than for the $^2T_{2g}$ level. The electronic spectra of the cobalt(II) and copper(II) complexes are then assigned as transitions from the minimum of the lower potential well to the upper potential energy surfaces. If the distortion is static, the nuclei are confined to the lower potential surface, but if the nuclear motion is such that coupling between the electronic process and the nuclear displacement can occur, it is impossible to specify the form of the ground state and a precise assignment of the electronic spectrum is not possible. The bands at 7500 cm^{-1} are considered to involve a transition between the lower and upper potential surfaces derived from the ^2E_g state and the band at 16,000 cm^{-1} as the transition from the lower potential surface of the ^2E_g state to the center of gravity of the potential surfaces originating from the $^2T_{2g}$ state.
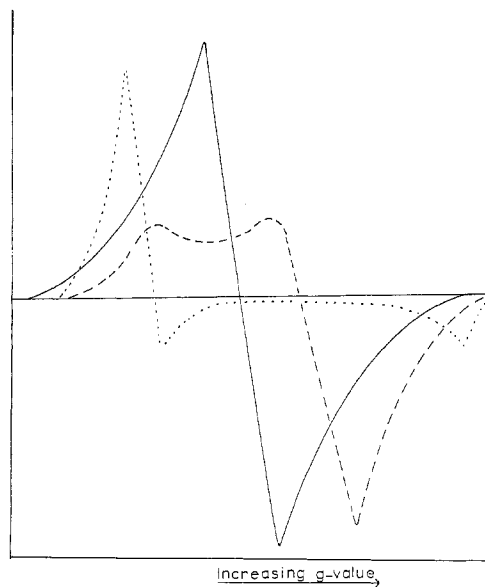
Electron Spin Resonance Spectra.—The electron

Figure 3.—The electron spin resonance spectra of K$_2$PbCu(NO$_2$)$_6$ at room temperature (———) and at the temperature of liquid nitrogen (– – – –), and the spectrum of K$_2$BaCu(NO$_2$)$_6$ at room temperature (. . . . .).

spin resonance spectra of all the paramagnetic hexanitrometallate(II) complexes have been recorded as powdered samples, all the cubic complexes giving isotropic g values (Figure 3), while the tetragonal barium– and calcium–copper complexes yielded anisotropic g values.

The ground state of the nickel(II) ion in an octahedral environment is $^3A_{2g}$, which should give rise to an isotropic g value of 2.00. However, spin–orbit coupling[34] may mix in the $^3T_{2g}$ excited state to produce the modified expression for the g value; $g = 2 - 8\lambda/10Dq$ to a first order in λ. In the hexanitronickelate(II) anion, the value of $10Dq$ has been shown to be 13,590 cm^{-1} and, using the free-ion value, -324 cm^{-1}, for λ the theoretical value of g is 2.19, which agrees closely with the observed values of 2.19 and 2.18 for the barium– and lead–nickel complexes, respectively. The most surprising feature of these results is the use of the free-ion value of the spin–orbit coupling constant. It is usually found necessary to use a reduced value, the value required for the hexaaquonickel(II) ion[35] being -270 cm^{-1}, a 17% reduction.

The electron spin resonance spectrum of the lead–copper complex gives an isotropic value of 2.10. The tetragonal copper complexes gave anisotropic g values, the approximate magnitudes[36] being $g_\perp = 2.050$ and 2.065 and $g_\parallel = 2.222$ and 2.240 for the barium–copper and calcium–copper complexes, respectively. The theoretical expressions for the g values for a copper(II) ion in an elongated tetragonal environment[37] are $g_\perp = 2 - 2\lambda/10Dq$ and $g_\parallel = 2 - 8\lambda/10Dq$, the experimental data yielding an approximate value of $2\lambda/10Dq$ of 0.05.

(30) H. B. Gray, "Electrons and Chemical Bonding," W. A. Benjamin, Inc., New York, N. Y., 1964, p 199.
(31) Reference 20, p 193.
(32) A. D. Liehr, *J. Phys. Chem.*, **67**, 389 (1963), and references therein.
(33) N. S. Ham, *Spectrochim. Acta*, **18**, 775 (1962).

(34) Reference 20, p 129.
(35) J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).
(36) V. S. Korolkov and A. K. Potapovich, *Opt. Spectry.*, **16**, 251 (1964), and references therein.
(37) Reference 20, p. 134.

Using a value of $10Dq$ of 12,600 cm^{-1} (see Electronic Spectra), an approximate value of λ of -315 cm^{-1} is obtained, giving a 62% reduction from the free-ion value of -829 cm^{-1}.

Compared with the anisotropic esr spectra of the tetragonal complexes, the isotropic spectra (at both X and Q band frequencies) found for the cubic lead–copper, lead–cobalt, and barium–cobalt complexes are unusual. While it is not unknown for copper(II) compounds, no further examples for cobalt(II) have been reported. The first reported isotropic g value for a compound was for the hexaaquocopper(II) hexafluorosilicate(IV) diluted in the isomorphous zinc complex.[38,39] The copper(II) ion is in a cubic environment, yielding an orbitally degenerate ground state, the degeneracy of which is not removed by the presence of a small trigonal component of the crystal field. The ion is, therefore, subject to a Jahn–Teller instability which is removed, not by a static distortion but by a rapid oscillation between three equivalent tetragonal distortions along the three cartesian coordinates relative to the trigonal axis (1,1,1). The dynamic nature of this distortion is considered to be responsible for the observation of an isotropic g value at room temperature,[40] which becomes anisotropic below 20°K. as the tetragonal distortions are trapped out.

More recently, a number of tris-chelate complexes of copper(II) have been shown to give anisotropic spectra at room temperature which become isotropic above room temperature.[41] Tris(ethylenediamine)copper(II) sulfate has been shown to have an isotropic spectrum at room temperature,[42] and the crystal structure[43] indicates an essentially regular octahedral coordination of the copper(II) ion by the six nitrogens, but the symmetry of the cation is lowered to D_3 by the $(-CH_2-)_2$ bridges of the ligand. This crystal structure rules out the possibility of three mutually perpendicular static tetragonal distortions and supports the presence of a dynamic distortion consistent with the observed isotropic g value.

It is of some interest to compare the numerical value of the isotropic g value obtained for the lead–copper complex at room temperature with the tetragonal g values obtained from the barium–copper complex, $g_\perp = 2.045$ and $g_\parallel = 2.222$, the latter yielding a value of $2\lambda/10Dq \approx 0.05$. If the same ratio of $2\lambda/10Dq$ is assumed for the evaluation of the isotropic g value of the lead–copper complex, then the theoretical expression[37] $g = 2 - 4\lambda/10Dq$ yields $g = 2.10$, in agreement with the observed value of 2.10, and suggests that the extent of the static tetragonal distortion of the tetragonal complexes is of the same magnitude as the dynamic tetragonal distortion of the cubic complex.

In view of the effect of temperature on the known examples of isotropic esr spectra for the copper(II) ion, the spectrum of the lead complex has been examined over a range of temperature and shown to be clearly anisotropic at the temperature of liquid nitrogen, Figure 3, but the form is entirely different from the room-temperature anisotropic spectrum of the barium–copper complex. The esr spectrum does not show a sharp transition from an isotropic to an anisotropic spectrum as the temperature is lowered, but a gradual change over the temperature range 20–0°; a similar effect was observed for tris(2,2'-dipyridyl)copper(II).[41] This low-temperature spectrum clearly shows that the dynamic distortion is no longer present in the lead–copper complex, but the different form of the anisotropy suggests that the distortion present might involve a compressed tetragonal distortion, rather than the elongated form that is present in the barium–copper complex. No specific information on this point was obtained from the low-temperature X-ray powder photograph, but this did show that the change in structure did occur between room temperature and $-38°$ and emphasizes that the dynamic form of distortion in the lead–copper complex is only just stable, with respect to the static distortion, at room temperature.

The g values for a compressed tetragonal distortion[37] are given by the expressions $g_\parallel = 2$ and $g_\perp = 2 - 6\lambda/10Dq$ and, using a value of $\lambda/10Dq = 0.025$, yield calculated values of $g_\parallel = 2.0$ and $g_\perp = 2.15$. The estimated g values for the lead–copper complex at the temperature of liquid nitrogen are 2.061 and 2.155, suggesting that a compressed tetragonal distortion is not present. Attempts to observe the esr spectra of the compressed tetragonal structures present in β-Cu(NH$_3$)$_2$Cl$_2$ and β-Cu(NH$_3$)$_2$Br$_2$[44] were unsuccessful as very broad absorptions were observed due to exchange broadening caused by the presence of halogen bridges in these complexes.

The cubic lead–cobalt and barium–cobalt complexes were shown to have isotropic g values equal to 2.10 and 2.09, respectively, and as the cobalt(II) ions in these complexes have ^2E_g ground states in octahedral environments, they are Jahn–Teller unstable and analogous to the copper–lead complex. What is surprising is that the observed g values are approximately the same for the cobalt(II) and for the copper(II) complexes as the same theoretical expression for the g value must apply, namely $g = 2 - 4\lambda/10Dq$. If it is assumed that the value of $10Dq$ will not differ significantly for the cobalt and copper complexes, then the values of g will depend very much on the value of λ, the free-ion values of which are -829 and -530 cm^{-1} for copper(II) and cobalt(II) ions, respectively.[45] The observed isotropic g values suggest that both free-ion values of λ are reduced in the complexes but that of the copper(II) ion has suffered a greater percentage reduction than that of the cobalt(II) ion. A referee has suggested

(38) B. Bleaney and D. J. E. Ingram, *Proc. Phys. Soc.* (London), **A63**, 408 (1950).

(39) B. Bleaney and K. D. Bowers, *ibid.*, **A65**, 667 (1952).

(40) A. Abragam and M. H. L. Pryce, *ibid.*, **A63**, 409 (1950).

(41) H C. Allen, G. F. Kokoszka, and R. G. Inskeep, *J. Am. Chem. Soc.*, **86**, 1023 (1964).

(42) R. Rayan and T. R. Reddy, *J. Chem. Phys.*, **39**, 1140 (1963).

(43) M. Cola, G. Giuseppeti, and F. Mazzi, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. Fis., Mat. Nat.*, **96**, 381 (1962).

(44) F. Hanic and I. A. Cakajdova, *Acta Cryst.*, **11**, 610 (1958).

(45) B. N. Figgis and J. Lewis, "Modern Co-ordination Chemistry," Interscience Publishers, New York, N. Y., 1960, Chapter 6.

that this is consistent with greater ligand admixtures to the metal orbitals in the case of the copper(II) ion. No esr data on any other octahedral spin-paired cobalt-(II) complexes are available for comparison.

Discussion

The dipotassium lead(II) hexanitrometallates(II) of iron, cobalt, nickel, and copper have face-centered cubic crystal structures and from their magnetic properties have zero, one, two, and one unpaired electrons, respectively. These results suggest that the transition metal ions in these complexes are in octahedral environments with ground-state electron configurations and terms $t_{2g}^6 e_g^0 (^1A_{1g})$, $t_{2g}^6 e_g^1 (^2E_g)$, $t_{2g}^6 e_g^2 (^3A_{2g})$, and $t_{2g}^6 e_g^3 (^2E_g)$ for the iron, cobalt, nickel, and copper ions, respectively. This series apparently provides the only known example of isostructural compounds with the above electronic configurations and it is of interest to examine the predictions that ligand field theory makes concerning them. In particular, the occurrence of spin-paired d^7 and d^9 ions, in a seemingly cubic environment, contradicts the prediction of the Jahn–Teller theorem.[28]

The unit cell dimension, a, for these complexes increases from iron to copper in this series and suggests that the metal–ligand distances vary in the order Fe < Co < Ni < Cu, rather than in the order found for high-spin complexes, *viz.*, Fe > Co > Ni < Cu.[46-48] This accords with the predictions of ligand field theory for low-spin complexes (Figure 4)[49] and is consistent with the decreasing attraction experienced by the ligands as electrons are added to the antibonding e_g orbitals, notwithstanding the accompanying increase in nuclear charge.

The electronic reflectance spectra of the nickel complexes are consistent with a regular octahedral environment, whereas those of the cobalt(II) and copper(II) complexes are more consistent with a tetragonal environment.

The existence of these cubic complexes of the cobalt-(II) and copper(II) ions suggests the possibilities (1) that the environment of each ion is tetragonal with the unique axis in one of three mutually perpendicular directions, the distribution of these directions throughout the lattice being random, (2) that the ion environments are undergoing a dynamic tetragonal distortion in three perpendicular directions in the lattice, or (3) that the statically distorted hexanitro anions are undergoing free rotation in the lattice. The observed systematic increase in the a values of the lead salts from iron to copper renders (3) unlikely, since free rotation of an axially distorted complex ion would be expected to lead to a greater effective radius than if the complex ion were octahedral.
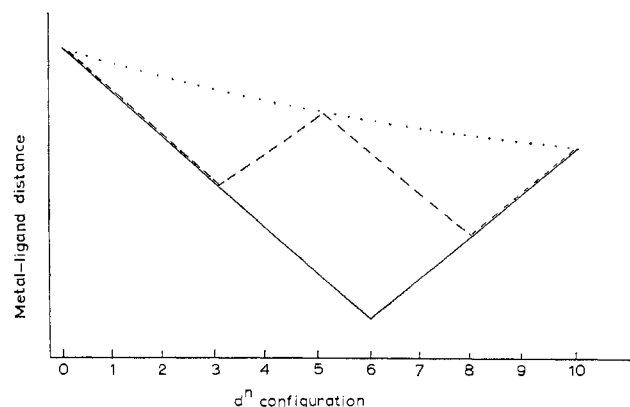
The electron spin resonance spectrum of the barium–

Figure 4.—The variation of metal–ligand distance in octahedral complexes as a function of the electron configuration, d^n, of the appropriate metal ions, as predicted by elementary ligand field theory (schematic): high-spin case (– – – –); low-spin case (———).

copper complex (Figure 3) is anisotropic and consistent with a local static tetragonal environment for the copper(II) ions in this tetragonal crystal. The spectrum of the lead–copper complex, however, is isotropic, and this rules out possibility (1) above as this would result in an anisotropic electron spin resonance spectrum, but it is consistent with possibilities (2) and (the less likely) (3) above. This dynamic distortion is best considered as a "pseudo-rotation" of the tetragonal environment of the copper(II) ions;[50] it is consistent with the observed cubic crystal structure and the tetragonal electronic spectrum as the former is a time-average property, whereas electronic processes are relatively fast and reflect the distorted environment in which the system spends the most time. The effect of lowering the temperature on the esr spectrum of the lead–copper complex suggests either that the vibrational energy of the "pseudo-rotation" has been so diminished as to allow the copper ion environments to "freeze out" with a static distortion along a particular crystal axis, or that the crystal structure of the complex has changed at the lower temperature for reasons unconnected with the Jahn–Teller effect. At this stage it is not possible to say which of these two effects is the correct explanation.

The properties of the cubic lead–cobalt and barium–cobalt hexanitro complexes are also interpreted as arising from a pseudo-rotational dynamic Jahn–Teller effect, and this is believed to be the first observation of this effect in a complex of the cobalt(II) ion.

(46) J. H. Van Santen and J. S. van Wieringen, *Rec. Trav. Chim.*, **71**, 402 (1952).

(47) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

(48) N. S. Hush and M. H. L. Pryce, *J. Chem. Phys.*, **26**, 143 (1957).

(49) *Cf.* B. M. Chadwick and A. G. Sharpe, to be published; D. A. Johnson and A. G. Sharpe, to be published.

(50) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304, (1958); V. Opek and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A238**, 425 (1957).

The Synthesis of Oxyhalides Utilizing Fused-Salt Media

BY RUSSELL S. DRAGO AND KENNETH W. WHITTEN[1]

In a molten equimolar lithium chloride–sodium chloride–potassium chloride mixture, anhydrous aluminum chloride has been found to react with several oxides or oxyanions of various nonmetals and high oxidation state transition metals to produce the corresponding acid chlorides. The compounds $VOCl_3$, $POCl_3$, $NOCl$, NO_2Cl, CrO_2Cl_2, $SeOCl_2$, CH_3COCl, and C_5H_5COCl were prepared. In several instances the yields or convenience of preparation exceed those realized in current synthetic methods.

Introduction

In 1939 Lux[2] presented a concept of acid–base behavior for fused salt media in which an acid was defined as an oxide ion acceptor and a base was defined as an oxide ion donor. The formal relationship between an acid and a base was represented as

$$base \rightleftharpoons acid + O^{2-}$$
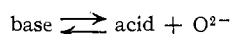
In a series of articles, Lux and Flood have developed and illustrated this concept of acid–base reactions which is generally known as the Lux–Flood theory.[3-6] In contrast to extensive studies involving physical measurements in fused salts[7,8] relatively little has been reported involving syntheses in these solvents. Spectroscopy in fused salts has indicated the existence of various complex species in these melts,[9,10] and the preparation of several coordination compounds has been reported.[11] Several interesting metathesis reactions have led to convenient syntheses.[12,13] Among the more interesting reactions in fused salts is the preparation of silane in 80% yield by treating a mixture of metallic aluminum and silicon dioxide, or any of a variety of silicates, in an aluminum chloride–sodium chloride eutectic with hydrogen under a pressure of 400 atm.[14]

Duke[15,16] has reported reaction kinetics in fused salts, and the results obtained in his work have provided suggestions for synthetic work. The reactions of dichromate and of pyrosulfate in nitrate melts are of particular interest because evidence for the existence of nitryl ions has been obtained from these investigations, *e.g.*

$$S_2O_7^{2-} + NO_3^- \rightleftharpoons NO_2^+ + 2SO_4^{2-}$$
$$NO_2^+ + NO_3^- \longrightarrow 2NO_2 + {}^1/_2O_2$$
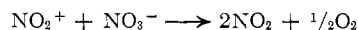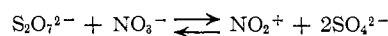
In the first step, equilibrium is established rapidly and the second step is slow. The order of the second step in nitryl ion is unity, and the order in nitrate ion cannot be determined because it is a part of the solvent. The pyrosulfate ion acts as a Lux–Flood acid in the above reaction,[15] by abstracting oxide ion from NO_3^-.

It was believed that cationic species such as the nitryl ion might be made to undergo reactions which could be utilized as preparative methods for compounds derived from this or similar cationic species. For example, the formation of nitryl ions in the presence of high concentrations of chloride ions should result in the formation of nitryl chloride. By analogy other oxychlorides could be prepared by forming oxygen-containing cations in the presence of chloride ions. In several instances, convenient, high-yield preparative methods have resulted.

Experimental Section

Reagent grade chemicals were used without further purification except as otherwise indicated. Nonhygroscopic solids were dried overnight at 110°, and hygroscopic solids were dried in a vacuum desiccator over anhydrous phosphorus(V) oxide. All transfers of chemicals were made inside a drybox.

The lithium chloride–sodium chloride–potassium chloride mixture was prepared by mixing together equimolar quantities of the anhydrous salts after the sodium chloride and potassium chloride had been dried overnight at 110°. Lithium chloride and

(1) Abstracted in part from the Ph.D. Thesis of K. W. Whitten, University of Illinois, 1965.
(2) H. Lux, *Z. Elektrochem.*, **45**, 303 (1949).
(3) H. Lux and E. Rogler, *Z. Anorg. Allgem. Chem.*, **250**, 159 (1942).
(4) H. Flood and T. Førland, *Acta Chem. Scand.*, **1**, 592, 781 (1947).
(5) H. Flood, T. Førland, and B. Roald, *ibid.*, **1**, 790 (1947).
(6) H. Flood and A. Muan, *ibid.*, **4**, 359, 364 (1950).
(7) B. R. Sundheim, "Fused Salts," McGraw-Hill Book Co., New York, N. Y., 1964.
(8) H. Bloom and J. O'M. Bockris, ref 7, pp 1–62.
(9) D. M. Gruen, ref 7, pp 301–336.
(10) E. Iberson, R. Gut, and D. M. Gruen, *J. Phys. Chem.*, **66**, 65 (1962).
(11) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Am. Chem. Soc.*, **83**, 2955 (1961); S. von Winbush, E. Griswold, and J. Kleinberg, *ibid.*, **83**, 3197 (1961); A. L. Plumley and W. C. Orr, *ibid.*, **83**, 1289 (1961).
(12) W. Sundermeyer, *Z. Anorg. Allgem. Chem.*, **313**, 290 (1961).
(13) W. Sundermeyer and O. Glemser, *Angew. Chem.*, **70**, 625 (1958); *ibid.*, **70**, 628 (1958).
(14) H. L. Jackson, F. D. Marsh, and E. L. Muetterties, *Inorg. Chem.*, **2**, 43 (1963).

(15) F. R. Duke and M. L. Iverson, *J. Am. Chem. Soc.*, **80**, 5061 (1958).
(16) F. R. Duke and S. Yamamoto, *ibid.*, **81**, 6378 (1959).