TABLE II

COMPARISON OF LIGAND FIELD PARAMETERS FOR
Ni(II) IN VARIOUS OXY ANION MELTS

Solvent	$-Dq,$ cm^{-1}	$B,$ cm^{-1}
Thallous acetate, 125°	736	913
Sodium acetate–potassium acetate eutectic, 250°	714	865
Lithium nitrate–potassium nitrate eutectic, 184°	774	884
Lithium sulfate–sodium sulfate–potassium sulfate, 550°	608	945

With respect to differences in the constituent cations of the melts, i.e., Tl$^+$ and K$^+$–Na$^+$, there is some difference in ligand field parameters in both systems. Whether this is due solely to temperature or whether the alkali acetate melt leads to poorer packing around the metal ion cannot be ascertained. There is no great difference between the thallium and potassium species except that Tl$^+$ is more polarizable. Na$^+$ is, of course, smaller and since it occupies 50% of the cation positions, it may have a structural influence, but the higher temperature should also reduce Dq.

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Magnetic Susceptibilities of Some Low-Spin Chromium(II) Complexes[1]

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The ligand field treatment of the magnetic properties of d^n configurations in octahedral complexes has been considered by many authors.[3-6] The theory has subsequently been extended to include the effects of small perturbations arising from trigonal or tetragonal components in the ligand field.[7-10] In general, such distortions have significant effects on the magnetic properties only for those systems possessing T ground states (in O$_h$ symmetry). Experimental tests of the theory have been made for most of the relevant d-elec-

tron configurations.[6-11] A configuration for which experimental data are lacking, however, is low-spin, octahedral d^4. Terezakis and Carlin[12] have studied the magnetic behavior of [Cr(bipy)$_3$]Br$_2 \cdot$4H$_2$O over the range 77–300°K, the only study of such systems with which we are familiar. The theory of Figgis, et al., was used to interpret the data. A reasonable fit of the data was obtained using an orbital reduction factor k of 0.6, an axial splitting parameter Δ of +640 cm^{-1}, a ^3F–^3P mixing parameter A of 1.3, and a complex:free ion spin–orbit coupling constant ratio λ/λ_0 of 0.74.

As part of a study of the magnetic properties of a variety of d^n systems, we have studied the magnetic behavior of four low-spin Cr(II) complexes of 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine over the temperature range 20–300°K. It is the purpose of this note to report these results.

Experimental Section

Preparations.—The preparation of the four compounds followed the same general procedure. The appropriate Cr(III) salt (bromide or perchlorate) was dissolved in water and electrolytically reduced to Cr(II). This solution was then transferred to an ethanolic solution of the ligand. The desired complex either precipitated almost immediately or upon addition of the sodium salt of the anion used. The solid was then removed by filtration, washed with cold ethanol, and dried under vacuum. The entire operation was carried out under nitrogen. At no time until the product was dry was it exposed to air. Analytical data are given in Table I. The data for the bipyridine bromide fit best for a dihydrate, although both anhydrous and tetrahydrate forms have been previously reported.[12,13]

Measurements.—Magnetic data were obtained using a Faraday balance as previously described.[14] Comparison of the calculated and experimental values were obtained by calculating experimental curves using different values of the parameters A, Δ, k, and λ.[15] The square of the difference between the calculated and experimental values was then the criterion used to arrive at the best fit.

Results and Discussion

The magnetic properties of the four complexes studied are shown in Figure 1. As is obvious from the plots, there is only a small decrease, approximately 0.1 BM, in μ_{eff} on cooling from 300 to 20°K. We have tried to fit the observed results to the theoretical calculations of Figgis, et al.[8a] We find it impossible to do so. The main reason for the lack of a good fit is the failure of the experimental values to drop, as the theory predicts they should, at low temperatures.

Figure 2 shows our attempt to fit the experimental data for Cr(bipy)$_3$Br$_2 \cdot$2H$_2$O. The bottom curve represents the calculated values for $A = 1.30$, $\Delta = 600$ cm^{-1}, $\lambda = -100$ cm^{-1}, and $k = 0.60$. These are the values of the parameters which give the best fit using the experimental data over the range 80–300°K only, and the fit is a reasonably good one. It is clear, however, that these values, which are quite close to those reported by Terezakis and Carlin,[12] do not

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(3) W. G. Penney and R. Schlapp, *Phys. Rev.*, **41**, 194 (1931); **42**, 666 (1932).

(4) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

(5) J. S. Griffith, "Theory of Transition Metal Ions," Cambridge University Press, London, 1961.

(6) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(7) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198, 204 (1961).

(8) (a) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc., A*, 1411 (1966); (b) *ibid., A*, 442 (1967); (c) *Nature*, **202**, 1138 (1964).

(9) R. M. Golding, K. F. Mok, and J. F. Duncan, *Inorg. Chem.*, **5**, 774 (1966).

(10) E. König and A. S. Chakravarty, *Theoret. Chim. Acta*, **9**, 151 (1967).

(11) B. N. Figgis, J. Lewis, and F. Mabbs, *J. Chem. Soc.*, 2480 (1960).

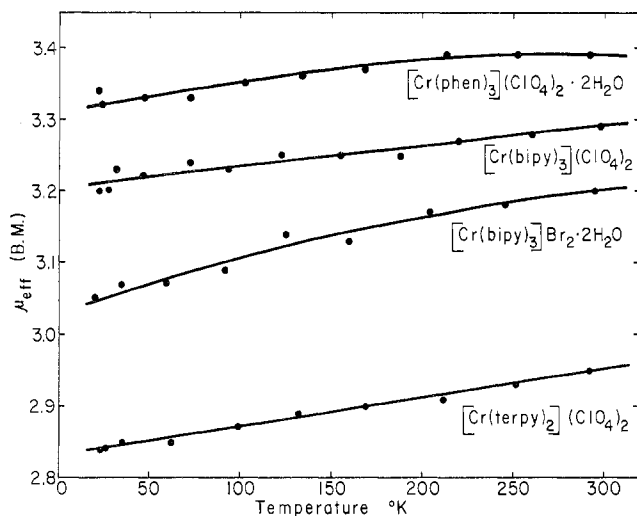(12) E. G. Terezakis and R. L. Carlin, *Inorg. Chem.*, **6**, 2125 (1967).

(13) A. Earnshaw, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. L. Carlin, and E. G. Terezakis, *J. Chem. Soc., A*, 511 (1966).

(14) J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, **1**, 68 (1967).

(15) The authors are deeply grateful to Dr. B. N. Figgis for supplying the computer program used to fit the data.

TABLE I
ANALYTICAL DATA

| | Elemental analyses, % | | | | | | | |
| | C | | H | | N | | Cr | |
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Cr(terpy)$_2$(ClO$_4$)$_2$	50.22	49.97	3.09	3.01	11.71	11.60	...	...
Cr(bipy)$_3$(ClO$_4$)$_2$	50.08	50.20	3.36	3.42	11.68	11.61	7.23	6.97
Cr(bipy)$_3$Br$_2$·2H$_2$O	50.29	50.03	3.94	4.24	11.73	11.46	...	...
Cr(phen)$_3$(ClO$_4$)$_2$·2H$_2$O	52.20	52.18	3.41	3.18	10.15	10.01	...	...

Figure 1.—Plots of μ_{eff} vs. T for low-spin Cr(II) complexes.

Figure 2.—Comparison of experimental (points) vs. calculated (solid lines) moments for Cr(bipy)$_3$Br$_2$·2H$_2$O.

reproduce the data at low temperatures. Using the data over the entire temperature range we obtain as a best fit the middle curve in Figure 2. This curve is calculated from the parameters A = 1.10, Δ = 400 cm^{-1}, k = 0.80, and λ = −50 cm^{-1}. The fit is obviously not a good one, the general temperature dependence not being reproduced. Similar results were obtained for the other compounds studied. We therefore conclude that the theoretical approach does not work well for the compounds studied and further that measurements limited to 80° can give misleading results.

Since the relative temperature independence of the moments could be due to a noncubic ligand field component which is too large for the perturbation techniques used in the calculations[8a] to be valid, we have also used an alternate approach. Figgis and Lewis have derived[6] eq 1 which is the expected magnetic moment for low-spin d^4 systems in the presence of a low-symmetry field component larger than the effects of spin–orbit coupling and temperature. The upper curve in Figure 2 shows that quite good agreement can

$$\mu_{eff}^2 = 8(1 - 8A^2k\lambda/3\Delta) + 4A^2k^2kT/\Delta \qquad (1)$$

be obtained using eq 1. The values used to calculate the solid line are A = 1.10, Δ = 1000 cm^{-1}, λ = −50 cm^{-1}, and k = 1.0. These are the values which give the best fit. They are generally reasonable except for the value of k which is disturbingly high. Similarly good fits can be obtained for the other compounds, but in each case one must use a large value of k or a small value of Δ (~500 cm^{-1}) to get good agreement. Since

the equation is derived assuming a large Δ, the latter situation is unreasonable, and since these compounds are expected to show a large amount of covalency, the former is suspicious.

Conclusions

There are a number of conclusions that can be drawn from this work. The first is that the theory developed by Figgis, et al.,[8a] is not applicable to these systems, perhaps because there is too much deviation from cubic symmetry.[16] This explanation draws some support from the fact that eq 1 gives an adequate fit of the data. The physical significance of the resulting parameters, however, is doubtful since either a small value of Δ or a large value of k results. Neither of these conditions seems reasonable for the compounds in question. Finally, we conclude that for low-spin Cr(II) and probably for many other systems data limited to 80° can give misleading results in the assignment of the various parameters inherent in the theory.

(16) G. N. La Mar and G. R. Van Hecke, *J. Am. Chem. Soc.*, **91**, 3442 (1969), have recently concluded from nmr measurements on some low-spin Cr(II) bipyridine and 1,10-phenanthroline complexes that there is an appreciable trigonal component to the ligand field and relatively little delocalization of the unpaired electrons.

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The Preparation of Nitrosonium β-Alumina

By R. H. Radzilowski and J. T. Kummer

In a previous paper[1] sodium β-alumina with the stoichiometric formula $Na_2O \cdot 11Al_2O_3$ has been reported to exchange completely its Na^+ ions for other cations (Ag^+, Tl^+, K^+, Rb^+, NH_4^+) in molten salts. The products of such ion exchanges have been used similarly to prepare other ion-substituted β-aluminas[1,2] (Ga^+, Li^+, In^+) which could not be made directly from sodium β-alumina. In all cases, the ion-substituted β-aluminas are isomorphous with the starting material, sodium β-alumina, and the exchanges are reversible. This paper reports the preparation of nitrosonium β-alumina by an ion-exchange method in which Ag^+ ions in silver-substituted β-alumina are replaced mole for mole by NO^+ ions in a $NOCl \cdot AlCl_3$ melt.

Experimental Section

The ionic compound $NOCl \cdot AlCl_3$[3,4] was prepared by placing 0.03 mol of $AlCl_3$ (Baker and Adamson Quality) into a quartz tube (60 cm long and 0.5 cm in diameter) and subliming it under an atmosphere of dry Ar to a cooled section of the tube. After sealing the tube under the sublimed $AlCl_3$, the tube was lowered into a Dry Ice–trichloroethylene bath. Nitrosyl chloride gas (The Matheson Co. Inc., East Rutherford, N. J.) was bled from a lecture bottle through Teflon and glass tubing into a Dry Ice cold trap where ~0.03 mol of NOCl was collected. The liquid NOCl was warmed gently until it distilled into the tube containing $AlCl_3$. After 1 hr in an ice bath and occasional agitation, the contents of the tube were heated gently to 200° in order to form the light yellow-brown melt of $NOCl \cdot AlCl_3$.

Silver-substituted β-alumina was made from 75–150-μ size single crystals of sodium β-alumina[5] that were heated in an NaCl melt at 810° for 16 hr. These crystals were washed with distilled water and heated to 400° before being placed in an $AgNO_3$ melt. Two exchanges in an $AgNO_3$ melt removed all but 0.08 wt % sodium.

The silver-substituted β-alumina crystals, preheated to 400° under Ar to remove any moisture, were inserted into the $NOCl \cdot AlCl_3$ melt and the tube was sealed with a small amount (~0.008 mol) of NOCl above the melt. The tube was heated at 197° for 23 hr. The melt to crystal volume ratio was ~20:1. Since $NOCl \cdot AlCl_3$ hydrolyzed readily, it was important that all materials were kept under anhydrous conditions. At the end of a run the melt was dissolved in distilled water giving off yellow-brown fumes and leaving a white precipitate and the transparent, yellow cast crystals of nitrosonium β-alumina. The precipitate

(1) Y. F. Yu Yao and J. T. Kummer, *J. Inorg. Nucl. Chem.*, **29**, 2453 (1967).

(2) R. H. Radzilowski, *Inorg. Chem.*, **8**, 994 (1969).

(3) H. Gerding and H. Houtgraaf, *Rec. Trav. Chim.*, **72**, 21 (1953).

(4) H. Houtgraaf and A. M. DeRoos, *ibid.*, **72**, 963 (1953).

(5) The β-alumina used was obtained from fused cast bricks (Monofrax H, 31 lb each) made by the Harbison Carborundum Co., Falconer, N. Y.

was dissolved in ethylenediamine and reprecipitated as AgCl. This precipitate was reduced on strong heating with Na_2CO_3 to Ag metal and then weighed. Although it was difficult to recover all of the silver due to the large amount of Cl^- ion in solution, the silver that was recovered showed that an essentially complete exchange occurred. After one exchange only <0.05 wt % Ag was detected in the crystals by X-ray fluorescence analysis.

It should be noted that larger silver β-alumina crystals (~1.5–2.5-mm diameter) could not be converted completely to nitrosonium β-alumina after one exchange even after 7 days in the melt. The melt to crystal volume ratio in these cases was ~80:1. When these 40%-exchanged crystals were sanded lightly on the edges and placed into a new melt, however, only 20% more of the Ag^+ ions left in the crystals could be exchanged for NO^+ ions. Apparently, the surface of the β-alumina crystals was attacked by the melt, NOCl, or $AlCl_3$, and the exchange was inhibited. The much smaller crystals could exchange their Ag^+ ions for NO^+ ions before their surfaces were corroded.

The crystals were analyzed for silver and sodium by atomic absorption spectroscopy using a Techtron AA (Cary Instruments Inc., Monrovia, Calif.). Infrared spectra of single crystals (0.75-1-mm diameter) of silver β-alumina and nitrosonium β-alumina were obtained on a Perkin-Elmer 457 grating infrared spectrophotometer using a beam condenser with KBr optics at 24°. X-Ray powder diffraction data were obtained with a Debye–Scherrer 114.59-mm camera. The samples were ground to 44-μ size, sieved, and packed into 0.3-mm glass capillaries. Samples were exposed to Ni-filtered Cu $K\alpha$ radiation for 0.7–6 hr on a Norelco X-ray generator. Intensities of reflections were measured on a double-beam recording microdensitometer (Joyce, Loebl and Co., Ltd., Gateshead, England). Thermogravimetric analyses were made on a 950 thermogravimetric analyzer (Du pont, Wilmington, Del.). The density was determined by weighing a 0.5-g sample in air and in freshly distilled chlorobenzene. The X-ray fluorescence analysis for silver was performed on a Norelco Universal vacuum X-ray spectrograph (Phillips Electronics Instruments, Mount Vernon, N. Y.).

Discussion

Nitrosonium β-alumina is isomorphous with the hexagonal layer structure of $Na_2O \cdot 11Al_2O_3$ which has the space group $P6_3/mmc$, with one molecule per unit cell. The lattice constants of $(NO)_2O \cdot 11Al_2O_3$ containing 6.13 wt % NO are $a_0 = 5.597$ and $c_0 = 22.711$ Å as determined from a Debye–Scherrer powder pattern and refined by a least-squares method. The powder diffraction pattern for nitrosonium β-alumina is given in Table I.

The variation of silver in silver-substituted β-alumina from sample to sample was in agreement with the 4.3–5.0 wt % sodium variation found in the starting material, sodium β-alumina. The amount of nitrosonium ion in the β-alumina structure was calculated from the chemical analysis for silver based on a mole for mole exchange for NO^+ ions since an accurate direct method of determining the nitrosonium ion content was not available. The calculated density and nitrosonium ion content of the stoichiometric $(NO)_2O \cdot 11Al_2O_3$ are 3.22 g/cm³ and 5.012 wt % NO, respectively. The measured density of nitrosonium β-alumina containing 6.13 ± 0.05 wt % NO is 3.22 ± 0.02 g/cm³.

The infrared spectra of single crystals of silver-substituted β-alumina and the nitrosonium β-alumina made from it are shown in Figure 1. A Nujol mull of a finely ground sample gave a much weaker absorption band