Schachtschneider's program GMAT.[10] Each of the five sets of Pb–Pb bonds was assigned a force constant and the F matrix was constructed. The G and F matrices were factored using C_2 symmetry coordinates constructed by standard group theoretical methods. The secular equation was solved using Schachtschneider's program FPERT.[10]

It was assumed the highest frequency mode, at 150 cm^{-1}, arises primarily from the short unique Pb(3)–Pb(4) interaction of 3.44 Å. An initial value of $f_{Pb(3)-Pb(4)}$ was estimated from the 150-cm^{-1} frequency and the diagonal G matrix element. This force constant was then used to evaluate the d_{ij} parameter in Badger's equation

$$r = d_{ij} + (c_{ij}/f)^{1/3}$$

where r is the internuclear distance, in ångströms, and f is the force constant in megadynes per centimeter. The parameter c_{ij} is about 0.5 for all heavy atoms, and its value is not critical in the calculation. Using the Pb(3)–Pb(4) distance and force constant, we obtained d_{ij} = 2.40 Å and used this value to determine the other Pb–Pb force constants. With these values held constant, $f_{Pb(3)-Pb(4)}$ was then adjusted to calculate the 150-cm^{-1} frequency exactly. The small change in $f_{Pb(3)-Pb(4)}$ required an insignificant change in d_{ij}. In this way all five force constants were fixed with one adjustable parameter. Their values are listed in Table I.

TABLE I

LEAD–LEAD DISTANCES AND ASSUMED FORCE CONSTANTS IN $Pb_6O(OH)_6^{4+}$

Interaction (see Figure 1)	Crystallographic distance, Å	Assumed distance (C_2 model)	f_{Pb-Pb}, mdyn/Å
Pb(3)–Pb(4)	3.44	3.44	1.09
Pb(5)–Pb(6)	3.67	3.67	0.62
Pb(1)–Pb(2)	3.67		
Pb(4)–Pb(5)	3.78	3.79	0.48
Pb(3)–Pb(5)	3.78		
Pb(2)–Pb(4)	3.79		
Pb(2)–Pb(5)	3.79		
Pb(2)–Pb(3)	3.80		
Pb(3)–Pb(6)	3.85	3.90	0.37
Pb(1)–Pb(4)	3.95		
Pb(1)–Pb(3)	4.09	4.09	0.26
Pb(4)–Pb(6)	4.09		

The twelve fundamental frequencies calculated by this set of force constants are compared with the observed frequencies in Table II. Considering the crudeness of the model, the over-all match is surprisingly good. It is clear that all of the frequencies could be calculated exactly by adjusting the individual Pb–Pb force constants within a reasonable range. The resulting values would have little significance, of course, since the actual force field must be vastly more complex than our model allows for. Our purpose here is merely to show that the resolved low-frequency Raman spectrum of $Pb_6O(OH)_6^{4+}$ is a reasonable consequence, within the simple cluster framework, of the actual arrangement of the lead atoms, taken together with Badger's rule.

TABLE II

LOW-FREQUENCY VIBRATIONS (CM^{-1}) FOR $Pb_6O(OH)_6^{4+}$

Obsd	Calcd	Symmetry type (C_2)	Obsd	Calcd	Symmetry type (C_2)
150	150	A	76	83	B
124	120	B	66	74	B
113	113	A	57	68	A
102	108	A	. . .	43	B
92	87	A	40	41	A
. . .	87	B	. . .	36	A

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[10] J. H. Schachtschneider, Technical Reports No. 231-64 and No. 57-65, Shell Development Co., Emeryville, Calif.

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Spectra of Cobalt(II) and Nickel(II) in Acetate Melts

BY R. A. BAILEY, M. ELGUINDY, AND J. A. WALDEN

Received May 19, 1969

The coordination geometry around transition metal ions dissolved in fused salts has been the subject of considerable interest.[1,2] The behavior of Co(II) in such media is particularly interesting, as both tetrahedral and octahedral geometries can be observed. Co(II) has been investigated extensively in fused halide media and to a lesser degree in oxy anion melts. In fused nitrates, Gruen[1,3,4] interpreted the spectrum on the basis of an octahedral species, while in fused sulfates, Johnson and Piper considered Co(II) to be tetrahedrally surrounded.[5] In both cases, interpretations were based chiefly on the band in the 18,000-cm^{-1} range, which is structured and can be ambiguous. In addition, extinction coefficients in both systems (in units of 1000 cm^2 M^{-1}) were *ca.* 100; compared to typical octahedral values near 10 and tetrahedral values near 500 for this ion with other ligand species.[1] Nickel(II) was octahedral in both of the above melts.[4,5] This report deals with further observations of Co(II) and Ni(II) in oxy anion melts, *i.e.*, molten acetates.

Experimental Section

Melt spectra were taken in stoppered quartz cells using a Unicam SP700 spectrophotometer and the heated cell compartment described previously.[6] Reflectance spectra were taken on a Beckman DU spectrophotometer equipped with a diffuse reflectance attachment and using powdered $MgCO_3$ as reference.

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TABLE I

COBALT(II) AND NICKEL(II) ACETATE SPECTRAL DATA

System	Peak position, cm^{-1}	Assignment	ε	$-Dq$, cm^{-1}	B, cm^{-1}	Geometry
Co(II) in thallous acetate, 150°	3,900	$^4A_2 \rightarrow {}^4T_2$	*Ca.* 15	−415	755	Tetrahedral
	7,200	$^4A_2 \rightarrow {}^4T_1$	18			
	16,100					
	17,300	$^4A_2 \rightarrow {}^4T_1(P)^a$	95			
	18,700					
Co(II) in sodium acetate–potassium acetate eutectic, 250°	3,940	$^4A_2 \rightarrow {}^4T_2$	*Ca.* 15	−405	770	Tetrahedral
	7,000	$^4A_2 \rightarrow {}^4T_1$	20			
	16,100					
	17,200	$^4A_2 \rightarrow {}^4T_1(P)^a$	100			
	18,800					
Co(II) in sodium acetate trihydrate, 90°	3,870	$^4A_2 \rightarrow {}^4T_2$	<10	−420	727	Tetrahedral
	7,500	$^4A_2 \rightarrow {}^4T_1$	25			
	17,400	$^4A_2 \rightarrow {}^4T_1(P)$	120			
	18,700					
Solid cobalt acetate (reflectance)	8,000	$^4T_{1g} \rightarrow {}^4T_{2g}$		904	754	Octahedral
	14,000	$^4T_{1g} \rightarrow {}^2E_g$				
	18,250	$^4T_{1g} \rightarrow {}^4A_{2g}$				
	19,750	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$				
Solid cobalt acetate tetrahydrate (reflectance)	8,400	$^4T_{1g} \rightarrow {}^4T_{2g}$		958	878	Octahedral
	14,500	$^4T_{1g} \rightarrow {}^2E_g$				
	18,700	$^4T_{1g} \rightarrow {}^4A_{2g}$				
	20,400	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$				
	21,500					
Ni(II) in thallous acetate, 125°	7,400	$^3A_{2g} \rightarrow {}^3T_{2g}$	1	736	913	Octahedral
	12,400	$^3A_{2g} \rightarrow {}^3T_{1g}$	1			
	23,400	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	6			
Ni(II) in sodium acetate–potassinm acetate eutectic, 250°	7,000	$^3A_{2g} \rightarrow {}^3T_{2g}$	1	714	865	Octahedral
	12,000	$^3A_{2g} \rightarrow {}^3T_{1g}$	2			
	22,400	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	13			
Solid nickel acetate (reflectance)	8,100	$^3A_{2g} \rightarrow {}^3T_{2g}$		760	953	Octahedral
	13,800	$^3A_{2g} \rightarrow {}^3T_{1g}$				
	24,800	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$				

[a] Band resolved into three components; ligand field parameters evaluated from center of gravity.

Thallous acetate (Eastman Organic Chemicals) was recrystallized from methanol. The liquid was almost colorless but with a brownish color developing after 3–4 hr. An equimolar mixture of anhydrous sodium and potassium acetates (Baker) approximates the eutectic composition; this melts at about 245° and is also moderately stable in the molten state. This mixture was dried according to the procedure of Hazlewood, *et al.*,[7] but chemicals taken directly from the reagent bottles yielded the same spectra. Sodium acetate trihydrate (Fisher) was used directly.

Anhydrous metal acetates were prepared from the reaction $MCO_3 + (CH_3CO)_2O \rightarrow CO_2 + M(CH_3COO)_2$, using hot acetic anhydride with added potassium acetate. The metal acetate–potassium acetate mixture was obtained by evaporation.

Analyses were carried out spectrophotometrically using nitroso-R salt for cobalt and dimethylglyoxime for nickel.

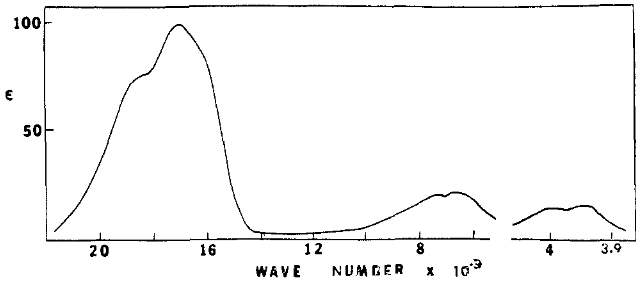

Figure 1.—The spectrum of cobalt(II) in molten thallous acetate at 150°.

Results and Discussion

Spectra of Co(II) in thallous acetate at 150°, in sodium acetate–potassium acetate eutectic at 250°, and in sodium acetate trihydrate at 90° are all similar in the visible region (Table I, Figure 1), both in terms of band positions and intensities. The latter are about the same as found in fused nitrates[1] and sulfates,[5] near 100 for the most intense peak.

Both the 18,000- and 7000-cm^{-1} bands can be assigned on the basis of either tetrahedral or octahedral geometry with reasonable values for the ligand field parameters; this is true also of the nitrate and sulfate spectra previously reported. The high-energy band is invariably found to be structured in tetrahedral geometry,[8] but this same structure can be accounted for in an octahedral geometry by overlap of the $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions and spin–orbit splitting of the latter.[8] Only the existence of the low-energy $^4A_2 \rightarrow {}^4T_2$ transition in tetrahedral geometry near 4000 cm^{-1} serves to establish with any confidence tetrahedral coordination. As shown in Table I and Figure 1, it was possible to detect such a band in the acetate solvents considered here. This band is absent

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in the Co(II)-free melts, which in any event were used as references. The extinction coefficients for this are only approximate, since the operation of the spectrophotometer under these conditions is far from ideal in this region. However, there is no doubt that this band is real and of similar intensity to the 7000-cm^{-1} band. (It was, however, indistinct in the trihydrate.) The narrowness may be due to the low-energy cutoff which limits the spectral range here. Ligand field parameters should be viewed with this in mind. Splitting of both these bands may be due to Jahn-Teller distortion. The ligand field parameters *Dq* and *B* were calculated using the data of Lever[9] and are given in Table I.

It is impossible to say if a significant amount of Co(II) remains in an octahedral environment in these melts, as the low extinction coefficient of an octahedral species, coupled with overlap from the strong tetrahedral bands, would make the former difficult to detect. The similarity of the spectra and the extinction coefficients in the two acetate melts, in sodium acetate trihydrate, and in the nitrate and sulfate melts suggests that a similar chromophore is present in all of them. It seems highly improbable that tetrahedral-octahedral mixtures would exist in such proportions as to give such similar extinction coefficients in these various situations even though the observed values are a factor of 5 lower than anticipated from analogy with the tetrahedral chloride species.[1]

For comparison purposes, diffuse reflectance spectra were taken of anhydrous cobaltous acetate and cobalt(II) acetate tetrahydrate, Table I. The former spectrum is seen to be quite similar to the melt spectra except that a new band makes its appearance centered at 14,000 cm^{-1}. A reasonable assignment of this band is $^4T_{1g}(F) \rightarrow {}^2T_{2g}(G)$. This has been interpreted on an octahedral model[10] with *Dq* of -925 cm^{-1} and *B* of 790 cm^{-1}. This geometry is indicated for the solid by the magnetism. Our values, Table II, are -904 and 754 cm^{-1}, respectively. It may be noted that this value of *Dq* is very close to that calculated from the tetrahedral melt value, assuming $Dq_{\text{oct}} = -{}^9/_4 Dq_{\text{tet}}$. On the other hand, if the melt were octahedral, a somewhat lower value of *Dq* would be expected for the solid (-840 cm^{-1}). However, *Dq* should decrease with increasing temperature as is shown by the difference between the thallous and alkali acetates, but the extent of this effect and the change of medium are impossible to estimate.

The spectrum of the hydrated cobaltous acetate shows a broadening of the high-energy band relative to the anhydrous salt. X-Ray crystallographic data[11] indicate that in the hydrated compound there are four coplanar water molecules surrounding the cobalt ion with two acetate species taking up the other two *trans* positions on the octahedron. Such an arrangement of ligands leads to a tetragonal distortion affecting the $^4T_{1g}(P)$ ligand field term. The broadness of this band is attributable to the lifting of the degeneracy of this term.

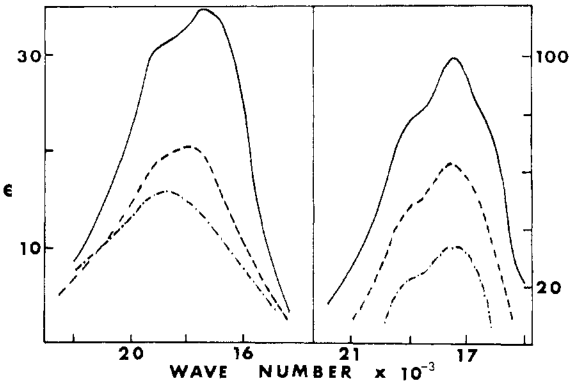

Figure 2.—The spectra of cobalt(II) in sodium acetate–water mixtures. Left, for $H_2O:CH_3COO^- = 12$: —, 90°; ---, 60°; —·—·—, 35°. Right, at 90°: —, $H_2O:CH_3COO^- = 3$; ---, $H_2O:CH_3COO^- = 6.6$; —·—·—, $H_2O:CH_3COO^- = 12$.

The spectrum of sodium acetate–water–cobalt(II) mixtures depends upon both the temperature and the water:acetate ratio, as is shown in Figure 2. With increasing temperature or acetate concentration the intensity increases while the bands shift to lower energies. Presumably in both cases this reflects an increase in the tetrahedral component which is present in small amounts even in room-temperature dilute aqueous solutions and which increases in amount with temperature, as shown by Suefelt and Connick.[12] In these solutions, as the temperature is increased, there may be a decrease in hydration of the acetate ions which results in their greater availability for coordination as has been suggested in halide cases.[13]

The nickel acetate systems (Table I) are most clearly octahedral; the assignments of the bands in Table I are in keeping with other Ni(II) systems.[1,5] The bands in the melt are of low intensity, but they are symmetrical and of a broadness comparable to the aqueous system. Parameters were evaluated from Lever's data.[9] Reflectance spectra of both anhydrous and tetrahydrated nickel acetate are similar to the solution spectra, and any inequivalency of ligands in the tetrahydrate does not seem to affect the symmetry of the field to any significant degree. The $^3A_{2g} \rightarrow {}^3T_{1g}$ transition is split in the anhydrous solid nickel acetate as it is in the hexaaquo complex; Liehr and Ballhausen[14] proposed that this is a consequence of spin-orbit coupling. The splitting of the band is reduced in the melts, especially at 250°, as the temperature effects blur this fine structure.

Table II gives a comparison of the ligand field parameters of Ni(II) in the oxy anion melts which have been studied. As can be seen, acetate is intermediate between SO_4^{2-} and NO_3^- in its strength, but the differences are not great.

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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.

Acknowledgment.—Support of this work by the National Science Foundation (Grant GP-8208) is most appreciated.

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

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Received May 23, 1969

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-electron 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 $[Cr(bipy)_3]Br_2 \cdot 4H_2O$ 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 $Cr(bipy)_3Br_2 \cdot 2H_2O$. 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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[1] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[2] (a) Petroleum Research Fund Fellow, 1968–1969. (b) NIH Predoctoral Fellow, 1966–1968. (c) To whom correspondence should be addressed.

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