TABLE V

OPTICAL ELECTRONEGATIVITIES FOR MF_6^{3-} COMPLEXES

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
χ_{opt}	2.22	2.25	2.39	2.65	2.91	3.01	3.06	3.23

shown in Table V are all appreciably larger than those deduced previously for these oxidation states. Thus, although in principal χ_{opt} should be independent of the nature of the ligand and of the coordination scheme, this bears out Jørgensen's[43] view that values obtained from tetrahalo and other species might be somewhat too low. The revised values incidentally greatly improve the correlation between χ_{opt} and the occupation number q, which previously[9] showed a considerable scatter. The plot of χ_{opt} *vs.* q gives now a slope of 0.165 unit (*ca.* 5 kK), which is consistent with its interpretation[43] as $E - A$, and compares with 0.15 unit (*ca.* 4.5 kK) for the M(IV) series (see Figure 7).

We have elsewhere[9] noted the existence of a strong connection between the optical electronegativity and the nephelauxetic ratio and have put forward a theoretical justification for this relationship. From a conceptual standpoint this connection is readily understood since both parameters essentially assess the same characteristic, namely, the ease of electron accession toward the central metal cation, and it is seen from Figure 8 that the plots of χ_{opt} *vs.* β for both the M(III) and M(IV) series for the fluoride ligand provide further evidence for this connection. Two points not previously noted[9] are worth attention. First of all, the value of χ_{opt} is extremely sensitive to small changes in β. This is not surprising since the essential proportionality is between χ_{opt} and a repulsion integral of the J(3d,3d) type, containing F_0, F_2, and F_4 Slater-Condon integrals. Thus, a small change in β, which reflects the F_2 and F_4 values, will have a substantial effect on F_0 and hence on χ_{opt}.

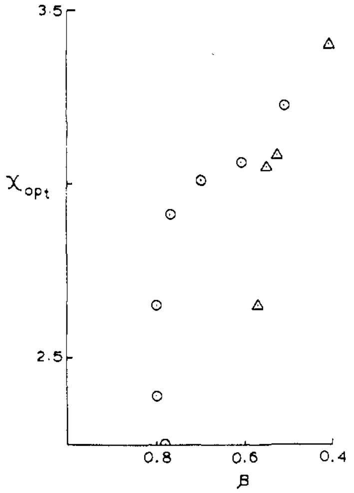

Figure 8.—Relationship between χ_{opt} and β for MF_6^{3-} and MF_6^{2-} anions: ○, M(III); △, M(IV).

Second, the fact that the relationship between β and χ_{opt} only becomes really apparent toward the end of the 3d series is also consistent: not only does the extent of covalency become much more marked near the end of the series, but the values of the B and the J(3d,3d) integrals also are known to increase in this sense.

Thus the investigation of the electronic spectra of the MF_6^{3-} species of the 3d series, completed in the present work, has confirmed the tendency for the nephelauxetic ratio to decrease toward the end of the series[8] and has provided further evidence for the dependence of χ_{opt} on the occupation number, q, of the 3d level and for the connection between χ_{opt} and β previously suggested.[9]

Acknowledgment.—We are much indebted to a referee for his helpful comments concerning the interpretation of the spectrum of K_3TiF_6.

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The Polarized Crystal Spectra of Tris(octamethylpyrophosphoramide)cobalt(II), -nickel(II), and -copper(II) Perchlorates[1]

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Polarized single-crystal electronic spectra of the tris-octamethylpyrophosphoramide complexes of cobalt(II), nickel(II), and copper(II) in the isomorphous crystals $M(OMPA)_3(ClO_4)_2$ have been measured at temperatures down to 5°K. The high energy of charge transfer and the low value of Dq combine to permit observation of all predicted spin-allowed and most spin-forbidden transitions. Trigonal electric dipole selection rules are clearly obeyed in the spin-allowed bands with only slight vibronic breakdown. The $Co(OMPA)_3^{2+}$ and $Ni(OMPA)_3^{2+}$ spectra at 5°K have been fitted to electrostatic ligand field calculations with the following results: for $Ni(OMPA)_3^{2+}$, Dq = 0.731 kK, B = 0.950 kK, C = 3.74 kK; for $Co(OMPA)_3^{2+}$, Dq = 0.765 kK, B = 0.855 kK, C = 3.68 kK; for $Cu(OMPA)_3^{2+}$, Dq = 1.0 kK. Trigonal splittings are apparently insignificant in the $Co(OMPA)_3^{2+}$ and $Ni(OMPA)_3^{2+}$ spectra. The spectrum of $Cu(OMPA)_3^{2+}$ yields an apparent v of 1.0 kK, although analysis in terms of lower symmetry is suggested.

Introduction

The study of intrinsically trigonal complexes and of metal ions in trigonal sites in single crystals using polarized crystal spectroscopy has been extensive during the last 10 years.[2] Included are the studies of trivalent

(1) Abstracted in part from the Ph.D. thesis of C. R. Taylor, Duke University, 1971. Presented in part at the Southeast Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969.

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metal ions doped into guanidiniumaluminum sulfate (GASH),[3,4] $AlCl_3$,[3,4] Al_2O_3,[5] $Al(acac)_3$,[6] and $NaMgAl(C_2O_4)_3 \cdot 9H_2O$,[7] as well as work on the pure crystals of salts of the tris-ethylenediamine[8-10] and hexaurea[11-13] complexes of trivalent ions. Investigations of divalent metal ions in trigonal fields have been much less extensive and include only the work on the 2,2′-bipyridine complexes[14] and tris(ethylenediamine)nickel(II) nitrate.[15] Only in the latter of these two are the results free from the possible complications of low site symmetry in the crystal and, thus, until this time there has been no unambiguous study of a series of divalent transition metal ions in a D_3 ligand field. Such a series exists in the perchlorate salts of the tris-octamethylpyrophosphoramide complexes of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II). This isomorphous series crystallizes in the trigonal space group $P\bar{3}c1$ with the metal ions occupying sites of D_3 symmetry and the C_3 axes of the complexes aligned parallel to the crystallographic *c* axis.[16,17] This offers a perfect opportunity for a critical testing of the ligand field and group theoretical predictions commonly used in justifying the results of polarized single crystal spectra, completely free of the complications of misalignment of chromophores, low site symmetry, and complicated birefringence effects.

We were especially interested in using the tris-OMPA complexes to extend our work on the spectra of trigonal nickel(II) and copper(II) compounds.[14,15] In this paper we report our spectral results for the perchlorate crystals of the tris(octamethylpyrophosphoramide)-cobalt(II), -nickel(II), and -copper(II) complexes.

An extensive series of metal ion complexes of octamethylpyrophosphoramide was originally reported by Joesten and coworkers.[18-20] These complexes are of interest, not only in trigonal field studies but also due to their possible use as models for the study of the interaction of metal ions with pyrophosphate sites in biological systems, *e.g.*, ATP and ADP.[21-23]

Experimental Section

Preparation of Complexes.—The complexes whose spectra are reported here were all prepared by methods previously reported.[18,19] Practical grade octamethylpyrophosphoramide (generously furnished by Pennsalt Chemical Co., Tacoma, Wash.) was distilled at 0.1 mm and the 110–120° fraction was taken for use. All other chemicals were standard reagent grade.

Growth of Single Crystals.—All crystals were grown from acetone under anhydrous conditions by slow evaporation. This was accomplished using a small flow of nitrogen gas through a plastic glove bag (I²R Co., Cheltenham, Pa.). All crystals were of a hexagonal prismatic habit.

Spectral Data.—All spectra were obtained using instrumentation, cryogenic equipment, and techniques previously described.[24] The procedures used for the analysis of the spectral data have also been outlined.[14,24] Both pure crystals and $Zn(OMPA)_3(ClO_4)_2$ crystals doped with the chromophores were used.

Computer Calculations.—All computer calculations were carried out on an IBM 360 System, Model 75, at the Triangle Universities Computation Center (TUCC), Research Triangle Park, N. C.

Results

Tris(octamethylpyrophosphoramide)nickel(II) Perchlorate.—The orthoaxial crystal spectra of $Ni(OMPA)_3(ClO_4)_2$ at 300 and 5°K are shown in Figure 1.

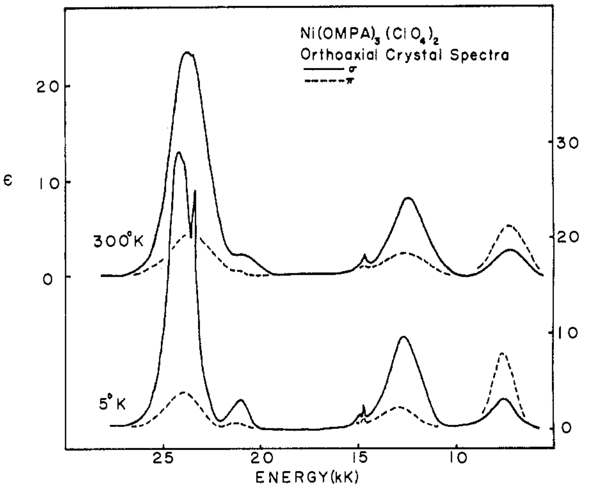

Figure 1.—Crystal spectra of $Ni(OMPA)_3(ClO_4)_2$.

Band maxima, molar absorptivities and integrated band intensities are summarized in Table I. The temperature dependence of the intensities of some bands as shown in Figure 1 and Table I is significant. The bands at 23.5 and 12.6 kK in the π polarization decrease in intensity on the order of 30–50% in going from ambient to liquid nitrogen temperatures, whereas the decrease in the σ-allowed bands is less than 15%. The band maxima and calculated energies are compared in Table II along with the "best fit" parameter values for *B*, *C*, λ, and *Dq*.

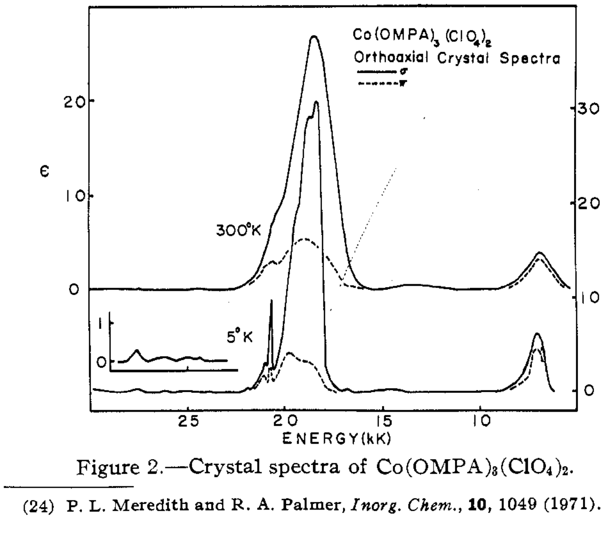

Figure 2.—Crystal spectra of $Co(OMPA)_3(ClO_4)_2$.

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TABLE I
INTENSITY DATA FOR $Ni(OMPA)_3(ClO_4)_2$ CRYSTAL SPECTRA

Excited state		300°K			80°K			5°K		
O_h	D_3	ν_{max}[a]	ϵ[b]	I[b]	ν_{max}	ϵ	I	ν_{max}	ϵ	I
$^3T_{1g}(P)$	$E(\sigma)$	23.6	23.4	2.47	23.9	29.8	2.16	24.0	28.7	2.10
	$A_2(\pi)$	23.5	4.6	0.50	23.9	3.8	0.33	24.0	3.6	0.32
$^3T_{1g}(F)$	$E(\sigma)$	12.3	8.5	1.58	12.6	9.7	1.36	12.7	9.7	1.35
	$A_2(\pi)$	12.5	2.6	0.54	12.90	1.9	0.28	13.0	1.9	0.31
$^3T_{2g}(F)$	$E(\sigma)$	7.20	2.8	0.69	7.30	3.4	0.71	7.40	2.6	0.65
	$A_1(\pi)$	7.25	5.3	1.38	7.35	7.5	1.36	7.45	7.4	1.34

[a] Units of kK. [b] Units of l. $mol^{-1} cm^{-1}$.

TABLE II
BAND MAXIMA OF $Ni(OMPA)_3(ClO_4)_2$ CRYSTAL SPECTRA

Excited state		Band max, kK			
			Obsd		
O_h	D_3	Calcd[a]	300°K	80°K	5°K
$^1T_{1g}(G)$	^1E	26.3			
	$^1A_2$				
$^3T_{1g}(P)$	^3E	23.9	23.6	23.9	24.0
	$^3A_2$		23.5	23.9	24.0
$^1A_{1g}(G)$	$^1A_1$	23.25	23.4	23.4	23.4
$^1T_{2g}(D)$	^1E	21.1	21.0	21.0	21.0
	$^1A_1$		21.0	21.0	21.0
$^1E_g(D)$	^1E	14.76	14.7	14.7	14.7
$^3T_{1g}(F)$	^3E	12.43	12.3	12.6	12.7
	$^3A_2$		12.5	12.9	13.0
$^3T_{2g}(F)$	^3E	7.34	7.20	7.30	7.40
	$^3A_1$		7.25	7.35	7.45

[a] Calculated using $Dq = 0.731$ kK, $B = 0.950$ kK, $C = 3.74$ kK, and $\lambda = -0.265$ kK ($B_0^+ = -15.4$ kK, $B_4^4 = -9.16$ kK)[23] and assuming octahedral geometry.

Tris(octamethylpyrophosphoramide)cobalt(II) Perchlorate.—The crystal spectra of $Co(OMPA)_3(ClO_4)_2$ are illustrated in Figure 2 and the band maxima, molar absorptivities, and integrated band intensities are summarized in Table III. Lowering the temperature to 80°K and below results in a splitting of the 18.6-kK band in both polarizations in addition to the resolution of several spin-forbidden bands and a sharpening of the broad, low-intensity band in the region of 14.0 kK. The assignments, band maxima, and calculated energies are listed in Table IV. The temperature dependence of the intensities is noted to be entirely analogous to that for $Ni(OMPA)_3(ClO_4)_2$.

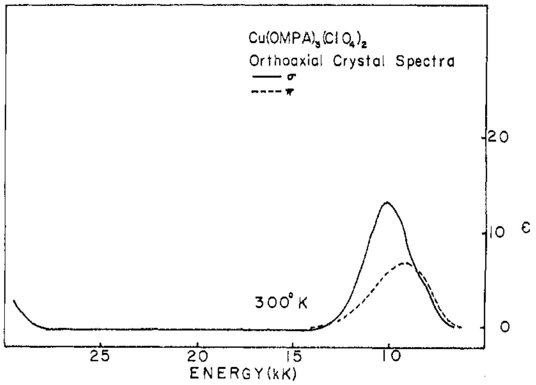

Figure 3.—Crystal spectra of $Cu(OMPA)_3(ClO_4)_2$.

TABLE III
INTENSITY DATA FOR $Co(OMPA)_3(ClO_4)_2$ CRYSTAL SPECTRA

Excited state		300°K			80°K			5°K		
O_h	D_3	ν_{max}[a]	ϵ[b]	I[b]	ν_{max}	ϵ	I	ν_{max}	ϵ	I
$^4T_{1g}(P)$	$E(\sigma)$	18.38	26.67	3.71	18.52	32.6	3.32	18.7	37.6	3.11
	$A_2(\pi)$	19.05	5.12	0.73	19.23	3.69	0.47	19.4	4.0	0.43
$^4T_{2g}(F)$	$E(\sigma)$	6.75	5.6	0.86	7.0	5.9	0.74	7.1	6.2	0.79
	$A_1(\pi)$	6.80	4.4	0.71	7.0	3.9	0.63	7.1	4.4	0.54

[a] Units of kK. [b] Units of l. $mol^{-1} cm^{-1}$.

TABLE IV
BAND MAXIMA OF $Co(OMPA)_3(ClO_4)_2$ CRYSTAL SPECTRA

Excited state		Band max, kK			
			Obsd		
O_h	D_3	Calcd[a]	300°K	80°K	5°K
$^2E_g(H)$	^2E	26.7	27.4	27.4	27.4
$^2T_{1g}(H)$	^2E	24.8		26.1	26.1
	$^2A_2$			26.1	26.1
$^2T_{2g}(H)$	^2E	22.7		24.0	24.0
	$^2A_1$			24.0	24.0
$^2T_{1g}(P)$	^2E	20.7	20.7	20.7	20.7
	$^2A_2$		20.7	20.7	20.7
$^4T_{1g}(P)$	^4E	18.8	18.4	18.5	18.7
	$^4A_2$		19.0	19.2	19.4
$^2T_{2g}(G)$	^2E	16.7		17.6	17.6
	$^2A_1$			17.6	17.6
$^2T_{1g}(G)$	^2E	16.1		16.7	16.7
	$^2A_2$			16.7	16.7
$^4A_{2g}(F)$	$^4A_2$	14.5	13.8	14.5	14.5
$^4T_{2g}(F)$	^4E	7.1	6.75	7.0	7.1
	$^4A_1$		6.80	7.0	7.1

[a] Calculated using $Dq = 0.745$ kK, $B = 0.855$ kK, $C = 3.68$ kK, and $\lambda = -0.165$ kK. Calculated values are centers of gravity of spin–orbit multiplets.

Tris(octamethylpyrophosphoramide)copper(II) Perchlorate.—The ambient-temperature single-crystal spectrum of $Cu(OMPA)_3(ClO_4)_2$ is shown in Figure 3 and band maxima are listed in Table V. Although the spectrum is that routinely expected for six-coordinate copper(II), the unusually low value of *Dq* and high energy of charge transfer make this complex as colorless to the eye as its zinc analog.[19] When the temperature of a single crystal of $Cu(OMPA)_3(ClO_4)_2$ is lowered to 80°K, the crystal becomes extensively cracked and virtually opaque. Although X-ray studies indicate that a recycling of the crystal to room temperature results in

TABLE V
BAND MAXIMA OF $Cu(OMPA)_3(ClO_4)_2$

Excited state		Band max, kK (300°K)
O_h	D_3[a]	
$^2T_{2g}$	$^2A_1$	10.2
	^2E	9.2

[a] Rhombic symmetry is suggested, but the data do not allow meaningful assignments in this lower symmetry (see text).

an apparent return to the original structure,[25] optical studies at cryogenic temperatures are not feasible. $Cu(OMPA)_3(ClO_4)_2$ is insoluble in the organic solvent mixtures commonly used to prepare glasses for work at liquid nitrogen temperatures.[26]

Discussion

Tris(octamethylpyrophosphoramide)nickel(II) Perchlorate.—The electronic configuration of nickel(II) is d^8 and the octahedral ground state is ${}^3A_{2g}$. The octahedral spin-allowed d–d transitions are, in order of increasing energy, ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$, ${}^3T_{1g}(F)$, ${}^3T_{1g}(P)$.[27] The band systems at 7.2, 12.3, and 23.5 kK are associated with these transitions (Figure 1). With a symmetry about the nickel ion of D_3, each of the triply degenerate octahedral levels will be split into an A and an E component by the trigonal field; $T_{2g} \rightarrow A_1 + E$ and $T_{1g} \rightarrow A_2 + E$. The necessary electric dipole selection rules in D_3 symmetry are then

$$A_2 \longleftarrow A_2$$

$$A_1 \xleftarrow{\pi} A_2$$

$$E \xleftarrow{\sigma} A_2$$

where π and σ refer to the orientation of the electric vector parallel and perpendicular to the C_3 axis of the molecule. The transitions can be assigned to an electric dipole mechanism from the observation that the axial and the σ spectra are coincident.[28]

Since the $Ni(OMPA)_3(ClO_4)_2$ crystal is isomorphous with its cobalt(II), copper(II), and magnesium(II) analogs, whose complete structures have been determined,[17] it is reasonable to assume that the nickel(II) ion resides at a site of exactly D_3 symmetry. Based on experience with other trigonal complexes of ions with orbitally nondegenerate ground states such as tris(oxalato)chromate(III),[7] a strict adherence to electric dipole selection rules by trigonal nickel(II) might be expected. However, in the only two complexes studied previously in detail, $Ni(bipy)_3{}^{2+}$ [14] and $Ni(en)_3{}^{2+}$,[15] some breakdown of the selection rules occurs. The metal ion in $Ni(OMPA)_3(ClO_4)_2$, as in $Ni(en)_3(NO_3)_2$, has D_3 metal ion site symmetry and, because of the high degree of electrostatic character of the bonding apparent in OMPA complexes, would seem an ideal additional test of the theory in the absence of possible π-bonding complications.[14,15]

The selection rules predict that absorption in the two higher energy band systems should be allowed only when the electric vector of the light is perpendicular to the C_3 axis of the complex. The intensity observed in the parallel components (${}^3A_2$) is definitely outside experimental uncertainty and represents partial breakdown of the selection rules even in this apparently ideal case. However, the extent of polarization is greater than in the $Ni(en)_3{}^{2+}$ [15] or $Ni(bipy)_3{}^{2+}$ [14] spectra. A reduction of temperature from 300 to 5°K results in a sharpening of the bands and a shifting of band maxima to slightly higher energies. The major source of this breakdown is apparent from the data in Table I. The decrease in intensity of the π components as the temperature is lowered is pronounced and far exceeds that of the σ components. Further, whereas the σ components increase in absorptivity as their half-widths decrease at lower temperature (typical of electronically allowed transitions), the absorptivities of the π components decrease. This clearly indicates that a vibronic mechanism is principally to blame for the failure of the polarization of the T_{1g} manifolds to be complete.[29–31] From the relation

$$I_T = I_0 \coth \frac{h\nu}{2kT}$$

Where I_0 and I_T are the integrated band intensities at 0 and T°K, the apparent frequency ν of the allowing vibration can be calculated.[24,32] Assuming a value for I_0 to be approximated by the integrated band intensity at liquid helium temperatures, the energy calculated for the allowing vibration was found to be 317 cm^{-1}.

As mentioned in connection with the lack of visible color in the copper complex, one of the most interesting aspects of the spectra of the tris-OMPA complexes is the very low value of Dq coupled with high energy of charge transfer. Under such conditions ligand field transitions usually unobservable should be well within reach. Further, the low value of Dq compared to other well-studied series should allow the confirmation of some previously uncertain spin-forbidden band assignments because of the unusual relative positions of intra- and interconfigurational transitions. Energy level calculations for the d^8 configuration[27,33] indicate that four singlet states (${}^1E_g(D)$, ${}^1A_{1g}(G)$, ${}^1T_{2g}(D)$, ${}^1T_{1g}(G)$) are at energies low enough to appear in the optical spectrum. Three of these appear in our spectra (Figure 1) and have been assigned in Table II. Of particular note in this regard is the assignment of the ${}^1E \leftarrow {}^3A_2$ transition to the well-resolved sharp, weak band at 14.65 kK. In other extensively studied systems such as $Ni(H_2O)_6{}^{2+}$ [34] and $Ni(bipy)_3{}^{2+}$ [14] this transition is virtually coincident with one or the other of the spin-allowed bands and somewhat ambiguous of assignment. However, its assignment in $Ni(OMPA)_3{}^{2+}$ is unmistakable. In this instance it fulfills exactly the predictions of its intraconfigurational parentage; its sharp (0–0) component is the most intense of a limited but distinct progression of vibronic components.

Actually two progressions appear distinguishable, the first in quanta of 250 cm^{-1} is then repeated 1220 cm^{-1} higher in energy. The 250-cm^{-1} vibration is likely a metal–oxygen stretch, whereas the other is very close in energy to an overtone of the phosphorus–oxygen vibration observed in the ir spectra of $M(OMPA)_3(ClO_4)_2$ compounds at 1200–1230 cm^{-1}.[20]

The location of the ${}^1E$ band just to higher energy of the ${}^3T_{1g}(F)$ manifold suggests that its vibronic analysis might be used, as was that of the ${}^1A_1$ band in $Ni(en)_3{}^{2+}$,[15] to confirm the vibronic mechanism as that responsible for the breakdown of the selection rules forbidding π intensity in the ${}^3T_{1g}$ manifold. Unfortunately the (0–0)

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component of ${}^1E$ in $Ni(OMPA)_3{}^{2+}$ appears in both polarizations. The temperature dependence of the π intensity indicates some vibronic mixing but apparently another mechanism is also active—perhaps spin–orbit coupling.

Trigonal splitting in the triplet–triplet bands appears to be smaller than it is possible to observe reliably from broad band maxima. The apparent splitting in ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ is due, we believe, to an instrumental artifact that occurs unfortunately exactly at the energy of the broad maximum. The small trigonal splitting is not unexpected considering the minimal distortion from octahedral symmetry revealed in the crystal structure.[17] Because of this situation we have fit the spectrum using an octahedral calculation.

The program used (DTWOSCH) has been described elsewhere.[24,35] The bands fit were the ${}^3T_{2g}(F)$, ${}^3T_{1g}(F)$, ${}^3T_{1g}(P)$, ${}^1E_g$, ${}^1T_{2g}$, and ${}^1A_{1g}$. The parameter values developed are listed in Table II. The value of λ was calculated from the ambient temperature magnetic susceptibility[18,30,36]

$$\chi = \frac{8N\beta^2}{3kT}\left(1 - \frac{4\lambda}{10Dq}\right) + \frac{8N\beta^2}{10Dq}$$

and held constant during the fitting process at -265 cm^{-1} or 84% of the free ion value.

Tris(octamethylpyrophosphoramide)cobalt(II) Perchlorate.—Cobalt(II) in the presence of octahedral fields has been extensively studied.[29,30,37–40] A complete energy level diagram for the d^7 electronic configuration in a field of octahedral symmetry assuming nonzero spin–orbit coupling has been published by Liehr.[41] Figure 2 illustrates the results of our single-crystal spectra of cobalt(II) in a field of near-octahedral symmetry. These spectra reveal two broad, distinct manifolds. The first, with a maximum at 6.8 kK, may confidently be assigned to bands associated with the first spin-allowed transition for the cobalt(II) ion in an octahedral field (${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$) consistent with previous observations.[29,37–41] We associate the intense band in the σ spectrum at 18.5 kK with components of the ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition assuming a very small apparent trigonal splitting. These two assignments permit the calculation of the parameters Dq and B of the parent octahedral field.[42] Taking 6.8 and 18.5 kK as the respective band energies, we obtain $Dq = -745$ cm^{-1} and $B = 855$ cm^{-1}.

The strong polarization of the ${}^4T_{1g}$ manifold indicates clearly that the ground state must be ${}^4A_2$. Some of the decrease in intensity of the π component of this band could be due to depopulation of the higher ${}^4E$ component of the ground state. If the E were lower, the polarization at ambient temperature would not be predicted to be very great and would *decrease* with lowering temperature.

From these assignments, then, the third spin-allowed transition, that to ${}^4A_{2g}$, should be symmetry forbidden as well as forbidden because of its two-electron character[43] in the strong-field limit. Careful subtraction from the $Co(OMPA)_3(ClO_4)_2$ spectrum of the spectrum of a $Zn(OMPA)_3(ClO_4)_2$ crystal of similar thickness reveals a broad, very weak band at 14.5 kK. This is almost certainly the ${}^4A_{2g}$ band. Its predicted position based on the energies of the other two spin-allowed bands would be 14.5 kK.

For reasons discussed earlier in connection with the discussion of the $Ni(OMPA)_3(ClO_4)_2$ spectrum, the spectrum of $Co(OMPA)_3(ClO_4)_2$ should be rich in spin-forbidden bands. In the absence of any evidence for significant trigonal splitting we can assign these bands in terms of their octahedral parentage. Of those bands listed in Table IV only the ${}^2T_{2g}(H)$, ${}^2T_{1g}(P)$, ${}^2T_{1g}(G)$, and ${}^2T_{2g}(G)$ excited states are associated with *intra*configurational transitions. Therefore the sharp spike at 20.65 kK should be assigned to the ${}^2T_{1g}(P)$ zero-phonon transition in rough agreement with its predicted position.[41] The structure observed in this band is essentially the same as that observed in the ${}^1E$ band of $Ni(OMPA)_3(ClO_4)_2$ and is clearly vibronic.

In addition to the bands assigned above, several other weak bands appear in the region above 21.0 kK and between 16 and 18 kK. In order to assign these bands on a rational basis a calculation was performed using a program (OCTAD37) written and generously provided by Dr. J. C. Hempel. This program uses a basis symmetry adapted to the octahedral double group. In the absence of a direct determination of λ, the empirical relationship $\lambda = 0.168B^2/Dq$ was used.[42] Assuming the correctness of the assignments of the ${}^4T_{2g}(F)$, ${}^4T_{1g}(P)$, and ${}^2T_{1g}(P)$ transitions above, best fit values for these bands were obtained by manually varying Dq, B, and C. From the resulting calculated energies, assignments of the other transitions were made as listed in Table IV. The assignments of the weak spin-forbidden bands were made with consideration of the prediction that *intra*configurational transitions will be sharper than *inter*configurational ones. For example the ${}^2T_{1g}(G)$ and ${}^2T_{2g}(G)$ transitions were assigned to the sharp peaks at 16.7 and 17.6 kK, respectively (Figure 2). It must be admitted that the assignments of these weak bands are not unambiguous. Other fits are possible, but any other than that listed in Table IV gives unfavorable results for the sharp, well-defined peak at 20.65 kK confidently assigned to the ${}^2T_{1g}(P)$.

Assignment of the doublets as described above leaves unexplained the additional structure in the major band centered at 19–20 kK. Attempts to fit the spectrum assigning this structure to quartet–doublet interaction were fruitless. The most likely explanation in light of the vanishingly small trigonal splitting observed in $Ni(OMPA)_3{}^{2+}$ is spin–orbit coupling effects. Another possibility is presumably Jahn–Teller splitting of the excited state. Similar structure is observed in almost all six-coordinate cobalt(II) spectra.[37–45]

Tris(octamethylpyrophosphoramide)copper(II) Perchlorate.—Copper(II) possesses a d^9 configuration and in the presence of an octahedral field should have a ${}^2E_g$ ground state. Thus, octahedrally coordinated copper(II) should display only one spin-allowed transition at $10Dq$. The complexes of copper(II) have re-

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cently been reviewed by Hatfield and Whyman[46] and by Hathaway and Billing.[47]

The complete cystal structure of tris(octamethylpyrophosphoramide)copper(II) perchlorate has previously been reported,[17] and the copper(II) site symmetry was found to be D_3 at room temperature. $Cu(OMPA)_3(ClO_4)_2$ is the second reported example in which the copper(II) ion resides at a site of D_3 symmetry in a crystalline compound (the other being $Cu(en)_3SO_4$[48]). Classically, this is equally as unexpected as copper(II) in a pure octahedral field since in either case the electronic ground state should be doubly degenerate (E or E_g). Analogous situations occur in the six-coordinate complexes of ions with the d^4 configuration. In such instances one expects to find evidence of some static or dynamic Jahn–Teller[49] distortions as a means of removing the apparent ground-state degeneracy.[50,51]

Spectroscopically these trigonal d^4 and d^9 complexes have been of interest because of the occurrence in some of them of an electronic transition in the infrared region far below that expected for the band associated with a basically octahedral complex with small trigonal distortion. Davis, Fackler, and Weeks[52] have reviewed the complexes of manganese(III) showing this low-energy band while Palmer and Piper[14] and Jørgensen[50] have discussed the only known d^9 instances, $Cu(bipy)_3^{2+}$ and $Cu(phen)_3^{2+}$. Explanations for these low-energy transitions have included static Jahn–Teller distortions (apparently excluded in the proven D_3 cases), charge transfer,[53] trigonal splitting,[14] and π bonding.[14]

The electronic spectrum of $Cu(OMPA)_3^{2+}$, both in solution and in single crystals of the perchlorate salt, exhibits a broad, slightly distorted band with a maximum at *ca.* 10 kK. If this is assigned as arising from transitions to levels associated with the $^2T_{2g}$ state in octahedral symmetry, an approximate Dq of 1.0 kK is obtained. This would seem a reasonable assignment in light of the very small distortions from octahedral symmetry revealed in the crystal structure and the vanishingly small trigonal splittings apparent in the spectra of the cobalt(II) and nickel(II) analogs.

A similar situation exists for the series $M(bipy)_3^{2+}$ [14] in terms of small observed trigonal splittings for the nickel(II) and cobalt(II) compounds. However, a very prominent, well-defined low-energy band appears in the spectra of both $Cu(bipy)_3^{2+}$ [14] and $Cu(phen)_3^{2+}$.[34] We have looked diligently in the region 3–5 kK for some evidence of a second transition in $Cu(OMPA)_3^{2+}$. No second band has been detected. In this respect $Cu(OMPA)_3^{2+}$ appears analogous to $Cu(en)_3^{2+}$.[54]

The association of the 10-kK band with the $^2T_{2g} \leftarrow {}^2E_g$ octahedral manifold fixes Dq. The polarized single-crystal spectra show reasonably strong-intensity anisotropy in this band (Figure 3) and a difference in σ- and π-band maxima of 1.0 kK. This splitting is outside experimental uncertainty and can be assigned to trigonal splitting, yielding a v of 1.0 kK. The shoulder at 9.2 kK is logically the σ component of the $^2E \leftarrow {}^2E$ band. This is an order of magnitude smaller than the apparent splitting in the $Cu(bipy)_3^{2+}$ spectrum.[14] The molar absorptivity of the σ band of 13.2 compares to 19 for $Cu(en)_3^{2+}$,[55] 54.5 for $Cu(bipy)_3^{2+}$,[14] and *ca.* 50 for $Cu(phen)_3^{2+}$,[34] again classing the OMPA complex with the ethylenediamine analog. Low-temperature optical spectra were not possible owing to the fact that the crystal of $Cu(OMPA)_3(ClO_4)_2$, unlike its nickel(II) and cobalt(II) analogs, becomes opaque at low temperature from the development of a myriad of minute cracks.

The appearance of a second shoulder in the σ spectrum at *ca.* 8.7 kK suggests the possibility that the effective symmetry is in fact lower than D_3. This would be in keeping with the predictions of the Jahn–Teller theorem. However, this region of the spectrum is complicated by numerous ligand vibrational overtones and polarizer absorptions making the location, and even the existence, of these shoulders somewhat questionable. Because of this uncertainty, as well as because of the multiplicity of possible splittings,[14] more detailed analysis of the data in, for example, C_2 symmetry does not seem profitable.

Because of the theoretical unlikelihood of truly trigonal copper(II), Joesten, Koch, Martin, and Venable[25] have investigated the ambient and cryogenic epr spectra of $Cu(OMPA)_3^{2+}$ in pure single crystals. Their data indicate that a dynamic Jahn–Teller distortion is probably in effect with the signal becoming anisotropic at *ca.* 95°K. (They found that Weissenberg photographs before and after cooling are identical in spite of the opacity of the crystals.) Such a finding is compatible with the axial symmetry exhibited by the optical spectrum in that the random distribution of the rhombic (Jahn–Teller) distortion would produce for the optical and X-ray diffraction experiments a time-averaged trigonal symmetry.

Somewhat contradictory evidence is obtained from a study of the anisotropy of the temperature factors in the diffraction data. Joesten, *et al.*, found that there is essentially no difference between the vibrational ellipsoids of the donor oxygens in the copper(II) complex and those in the analogous cobalt(II) and magnesium(II) complexes.[17] A similar situation was found for the $Cu(en)_3SO_4$ thermal ellipsoids.[48] The donor nitrogen ellipsoids were found to differ only slightly from the non-Jahn–Teller susceptible $Ni(en)_3SO_4$ analog. One must conclude from this that the distortions sensed by the epr spectrometer either are nuclear distortions beyond the range of detection by X-ray diffraction or involve primarily the bonding electron density rather than the nuclear framework. Low-temperature diffraction data might be valuable in reaching a conclusion in this matter.

With four examples now of formally trigonal copper(II) it is appropriate to ask again what promotes this seemingly unlikely state and in particular what produces in some of the compounds, but not in others, a second, lower energy, electronic transition. The most obvious difference between the α-diimine ligands on the one hand and ethylenediamine and OMPA on the other is

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the extent of delocalized π bonding. Numerous experimental techniques have illustrated the importance of delocalized bonding in the α-diimines and even more pertinently in their metal complexes.[56] Delocalized bonding can be considered minimal in aliphatic amine ligands such as ethylenediamine. The fact that the planarity of the OMPA chelate ring found in $Cu(OMPA)_3(ClO_4)_2$ is also found in $Co(OMPA)_3(ClO_4)_2$ and $Mg(OMPA)_3(ClO_4)_2$ indicates a lack of significant dπ–pπ bonding in this trigonal copper complex. Further, the lengths of the bonds found in the chelate ring do not support a significant π-bonding contribution in these complexes.[17] It would appear that π-bonding effects are the most likely source of the appearance of low-energy ligand field bands in the near-infrared spectrum, although the exact nature of these transitions remains in question.

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A Direct Proton Magnetic Resonance Cation Hydration Study of Lanthanum, Zinc, Cerium, Iron, and Nickel Perchlorates and Erbium Nitrate in Aqueous Solution

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A cation hydration study of diamagnetic $La(ClO_4)_3$ and $Zn(ClO_4)_2$ and paramagnetic $Ce(ClO_4)_3$, $Er(NO_3)_3$, $Fe(ClO_4)_2$, and $Ni(ClO_4)_2$ in aqueous solution has been carried out by a direct proton magnetic resonance (pmr) method. The technique is based on the ability to slow ligand and proton exchange thereby permitting the observation of separate resonance signals for bound and bulk water molecules. Temperatures required for study varied from −30° for Ni^{2+} to −120° for Zn^{2+} and they were made possible by dilution of the aqueous solutions with acetone and, when necessary, Freon 12. Area integrations led to hydration numbers of 6 for all cations except Er^{3+} which was involved in extensive complex formation and could not be studied in great detail. Spectral evidence for inner-shell complex formation also was obtained in the Ce^{3+} solutions leading to the possibility of a greater maximum hydration number than 6 for this species.

Introduction

During recent years, direct oxygen-17[1-7] and proton magnetic resonance (pmr)[8-15] methods have been applied to cation hydration studies in aqueous solution and aqueous solvent mixtures. The success of these experiments lies in the ability to slow ligand and proton exchange thereby permitting the direct observation of a resonance signal for water molecules in the cation solvation shell. When this is possible, area evaluations lead to accurate measurements of cation hydration numbers,[1-15] competitive solvation,[8] and complex formation.[12-15] Species studied by oxygen-17 and proton magnetic resonance spectroscopy include Al^{3+}, Be^{2+}, Ga^{3+}, Co^{2+}, Ni^{2+}, Pt^{2+}, and Pt^{4+},[1-9,11] while pmr studies alone have been made for Mg^{2+}, In^{3+}, Sc^{3+}, Y^{3+}, Th^{4+}, UO_2^{2+}, Sn^{4+}, and Zn^{2+},[10,12-15] the last in a preliminary manner.

Several of the ions to be described here have been studied by a variety of methods including Raman[16-19] and electronic absorption[20-24] spectroscopy of aqueous solutions, and analytical, conductometric, and spectroscopic measurements of crystalline complexes.[25-33]

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