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Magnetic and Spectral Properties of the Pentagonal-Bipyramidal Complex Ions Chloroaqua- and Diaqua[2,6-diacetylpyridine bis(semicarbazone)]cobalt(II)

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Principal crystal susceptibilities throughout the temperature range 10–300 K have been measured for the complexes $[Co(DAPSC)Cl,H_2O]^+Cl^- \cdot 2H_2O$ and $[Co(DAPSC)(H_2O)_2]^{2+}(NO_3^-)_2 \cdot H_2O$, where DAPSC = 2,6-diacetylpyridine bis(semicarbazone). Unpolarized, single-crystal transmission spectra have been recorded in the UV, visible, and near-IR regions. For each complex independently, the spectral and magnetic properties have been quantitatively and simultaneously reproduced within the angular overlap model (aom). Spectral bands in the 15 000–18 000-cm^{-1} region are assigned to components of the → ^{4}P manifold. Ligand field, aom parameters accurately reproducing spectral features and all magnetic properties all appear chemically sensible, commenting upon the normality of the axial bonds in these pentagonal-bipyramidal complexes and on the σ-bond characteristics of the keto group. Small differences in the spectra and magnetism of the diaqua and chloroaqua complexes are uniquely associated with a lesser π-donor ability of water with respect to chlorine.

Introduction

It has been argued recently[1] that extensive developments in the procedures of magnetochemistry, in particular the application of the angular overlap model (aom) to the magnetic anisotropies of low-symmetry molecules, have conferred upon the technique the possibility, lost for some years, of commenting directly on bonding in a manner significant to the nonspecialist chemist. These methods are applied in the present study to the interpretation of the single-crystal paramagnetic susceptibilities and transmission spectra of two seven-coordinate molecules which are members of series prepared and characterized by Palenik and Wester.[2] The essential pentagonal-bipyramidal stereochemistry about the central metal atom—here cobalt(II)—results from pentacoordination from the nearly planar ligand 2,6-diacetylpyridine bis(semicarbazone), DAPSC, and two axial ligands bonding perpendicular to the equatorial, pentagon plane. We report here studies on two systems in which the axial ligands are either both water molecules[3] or one water and one chlorine atom.[2,4]

Of immediately obvious interest is the nature of the pentagonal-bipyramidal ligand field in these complexes and its manifestation in the electronic spectrum.[5] Associated with this must be a curiosity as to how well the angular overlap model may be applied to such a high symmetry complex, albeit only of idealized D_{5h} symmetry, and more importantly how adequately we may locally parameterize the influence of four or five distinct donor atom types. From the outset, the present systems do not appear to lend themselves readily to a detailed ligand field analysis of local influences—which is the whole point of the angular overlap method—and hence one aim of this study is to test the method in these circumstances.

Experimental Section

The pentadentate ligand 2,6-diacetylpyridine bis(semicarbazone), DASPC, was prepared by dissolving a stoichiometric mixture of diacetylpyridine and semicarbazide hydrochloride in ethanol. The compound of stoichiometry DAPSC, $CoCl_2$, $3H_2O$, containing the complex ions $[Co(DAPSC)Cl,H_2O]^+$, was prepared by dissolution of cobalt chloride in an ethanol–water mixture and addition to an ethanolic solution of the Schiff base. The resulting precipitate was stirred in situ and heated to ca. 80 °C for 24 h, after which the precipitate was dissolved in water and the solution concentrated before cooling. The second cobalt complex, of stoichiometry DAPSC, $Co(NO_3)_2$, $3H_2O$, containing the complex ions $[Co(DAPSC)(H_2O)_2]^{2+}$, was prepared analogously by using cobalt nitrate instead of cobalt chloride. Suitable crystals for the magnetic and spectroscopic experiments were grown by slow evaporation at room temperature of these solutions. The $[Co(DAPSC)Cl,H_2O]^+$ complex was obtained as dark red thick plates while crystals of the $[Co(DAPSC)(H_2O)_2]^{2+}$ complex formed orange-red rods. Satisfactory analyses were obtained (Table I).

Susceptibility measurements were made on crystals weighing 1–3 mg, accurately oriented by standard X-ray oscillation and Weissenberg techniques. Crystals of both compounds are monoclinic but not isomorphous.[3,4]

Measurements were carried out with a Faraday magnetometer (Oxford Instruments), similar to that described in the literature[6] but using a continuous flow cryostat for measurements in the temperature range 10–300 K. The instrument was calibrated by using manganese Tutton salt. This standard was also used to check the position of the crystal in the sample chamber when no anisotropy greater than 1% was observed on rotation of the magnet throughout the complete angular range. Crystals of less than 1 × 2 × 3 mm were used throughout the measurements, ensuring that the samples lay entirely within the region of homogeneous force.

For each system, the three principal crystal susceptibilities χ_1 and χ_2 ($\chi_2 > \chi_1$ by convention) in the *ac* plane and χ_3 parallel to *b* were determined from different orientations according to procedures described elsewhere.[7] Reproducibility was checked for each complex as follows: (i) χ_1 and χ_2 were measured throughout the temperature range for two different crystals oriented along *b*. (ii) χ_3 was measured first on a crystal mounted parallel to *a*, together with $\chi_{c'}$, the susceptibility perpendicular to the *ab* plane, and then from a second crystal oriented along *c*, also giving $\chi_{a'}$ perpendicular to the *bc* plane. Separately determined values obtained for one principal crystal susceptibility agreed to better than 3%.

The angle ϕ subtented by χ_1 and *a*, measured from *a* toward *c*, was determined within 5° by direct observation and from the formula[8]

$$\sin^2 (\beta - 90° - \phi) = (\chi_{a'} - \chi_1)/(\chi_2 - \chi_1) \qquad (1)$$

where β is the monoclinic angle. The results of these determinations, performed at several temperatures throughout the range and found to vary insignificantly with temperature, are as follows.

	ϕ, deg	
	direct observn	deduced, from eq 1
$[Co(DAPSC)Cl,H_2O]^+$	75	67
$[Co(DAPSC)(H_2O)_2]_2^{2+}$	40	31

A gross diamagnetic correction has been applied to all results based on a measured value of −170 × 10^{-6} cgsu for the isomorphous $[Zn(DAPSC)Cl,H_2O]^+$ system. In Table II are collected interpolated experimental principal crystal susceptibilities and mean moments throughout the temperature range for both cobalt complexes. The obviously different results for the two compounds reflect the different molecular orientations obtaining in these quite different crystal structures.

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Table I. Elemental Analyses

	% Cl		% C		% H		% N	
	calcd	found	calcd	found	calcd	found	calcd	found
(DAPSC), $CoCl_2$, $3H_2O$	15.41	15.52	28.63	28.60	4.55	4.55	21.26	21.32
(DAPSC), $Co(NO_3)_2$, $3H_2O$			25.68	25.62	4.08	4.23	24.51	24.38

Table II. Observed, Interpolated Principal Crystal Susceptibilities χ (cgsu × 10^4; 1 cgsu ≡ $4\pi \times 10^{-6}$ m^3 mol^{-1}) and Mean Moments (μ_B)

	$[Co(DAPSC)Cl, H_2O]^+Cl^-\cdot 2H_2O$				$[Co(DAPSC)(H_2O)_2]^{2+}(NO_3)_2^{2-}\cdot H_2O$			
T/K	χ_1	χ_2	χ_3	$\bar{\mu}$	χ_1	χ_2	χ_3	$\bar{\mu}$
20	230	1305	1158	3.79	162	1170	972	3.51
40	148	726	652	4.03	128	712	616	3.94
60	130	480	448	4.11	121	480	442	4.08
80	108	354	336	4.12_5	114	360	330	4.14
100	106	274	267	4.15	102	280	265	4.15
120	96	226	222	4.17	94	232	218	4.17
140	88	194	190	4.20	84	198	185	4.17_5
160	80	170	166	4.21	77	174	162	4.20
180	72	150	146	4.20	70	154	145	4.21
200	67	134	130	4.20	65	136	130	4.20
220	62	120	118	4.19	61	124	118	4.21
240	57	109	108	4.19	57	112	110	4.22
260	53	100	99	4.18	52	103	99	4.20
280	50	94	94	4.21	50	96	92	4.21_5
300	48	88	88	4.23	46	90	85	4.20_5

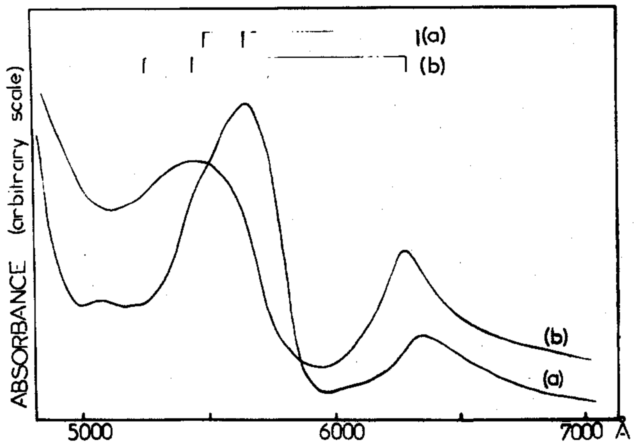

Figure 1. Transmission spectra of cobalt–DAPSC complexes (80 K): (a) $[Co(DAPSC)Cl,H_2O]^+Cl^-\cdot 2H_2O$, (b) $[Co(DAPSC)(H_2O)_2]^{2+}(NO_3^-)_2\cdot H_2O$. Energies of peak positions are given in the text and Tables III and IV.

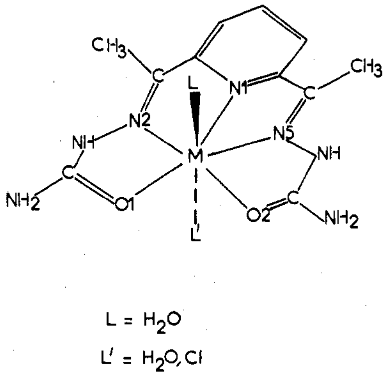

Figure 2. Numbering of DAPSC donor atoms.

The electronic absorption transmission spectra of single crystals of both complexes were recorded at room temperature and ca. 77 K by using a Cary 14 spectrophotometer. The strong color of the crystals required spectra to be recorded by using very thin samples. Only a little improvement in spectra resolution occurred on cooling, those shown in Figure 1 corresponding to the lower temperature.

Discussion

Calculations of eigenvalues, eigenvectors, and magnetic properties have been performed within the complete spin-quartet basis $^4P + {}^4F$ of the d^7 configuration by using techniques described elsewhere.[9] Donor atoms were placed at coordinates given by the appropriate X-ray analyses[3,4] and the parameter list following refers to the numbering scheme given in Figure 2. Apart from their detailed coordinates, donor atoms N2 and N5 are presumed chemically equivalent, as are O1 and O2. As the two axial ligands lie opposite one another and so cannot be distinguished by the aom, their influence is represented by average σ and π parameters. This is valid insofar as the taking of a cylindrically symmetric Co–water π bond is acceptable, as is assumed in the interests of minimal parameterization. We therefore consider the following ligand field parameters: for N1 e_σ, $e_{\pi\perp}$, $e_{\pi\parallel}$ (expected = 0), for N2,5 e_σ, $e_{\pi\perp}$, $e_{\pi\parallel}$ (expected = 0), for O1,2 e_σ, $e_{\pi\perp}$, $e_{\pi\parallel}$, for Cl,H_2O e_σ, $e_{\pi av}$, where $\perp$ and $\parallel$ refer to π bonding perpendicular and parallel to the pentadentate plane. We thus consider four ligand types with 11 aom parameters: in addition we have as usual B, ζ, and k for interelectron repulsion, spin–orbit coupling, and orbital reduction effects. We cannot expect to establish unique values for all these parameters and later we shall discuss the problems of parameter correlation. As ever in these studies the problem of exploring parameter space for fits to experiment is about as difficult as the presentation of the results of that exploration. The exposition now given has emerged after several spiral approaches to the problem.

Initially we have performed calculations within limited ranges of these parameter values, viz., $e_\sigma(N) \sim e_\sigma(O) \sim 4000$ cm^{-1}, $e_\sigma(Cl/H_2O) \sim 2000–5000$ cm^{-1}, $e_{\pi\perp}(N1) = -200$ to $+200$ cm^{-1}, $e_{\pi\perp}(N2,5) = 500–1500$ cm^{-1}, $e_{\pi\perp}(O) = 300–2500$ cm^{-1}, and $e_{\pi\parallel}(O) = 0–900$ cm^{-1}; other e_π parameters were set to zero; $B \sim 700–1100$ cm^{-1}, $\zeta \sim 400–550$ cm^{-1}, and $k = 0.3–1.0$. Excellent agreement with the observed principal susceptibilities over the complete temperature range could be obtained for several, but by no means all, combinations of these parameter values. Reproduction of the electronic spectra was more exacting.

The spectra of both chloroaqua and diaqua complexes are shown in Figure 1 and are closely similar. The bulk of the following discussion relates to the more resolved spectrum obtained for the chloroaqua complex. We presume the very weak feature at 19 700 cm^{-1} represents a spin-forbidden transition; further, a weak and very broad feature in the infrared region near 6000 cm^{-1} of the spectrum is ill-defined and insufficiently informative for present analysis. The tail in the ultraviolet region at energies greater than ca. 20 000 cm^{-1} is probably assignable to charge-transfer and/or ligand transitions, but this we discuss. The informative part of the spectrum thus consists of a band at ca. 15 800 cm^{-1} and a broader band with a shoulder centered at ca. 18 000 cm^{-1}, the splitting being of the order of 500 cm^{-1}.

Our analysis considers whether all spin-allowed d–d bands lie at energies less than 20 000 cm^{-1} or whether the "charge-transfer tail" actually masks further spin-allowed d–d transitions. We include the question of whether or not the bands at 15 800 and 18 000 cm^{-1} involve components of the ^4F free-ion term. We observe immediately that components of the ^4P term can only be calculated to lie higher than 20 000 cm^{-1} relative to ground if two conditions are satisfied. First, we would require a large value for the Racah B parameter, against which we see no objection provided it is not significantly greater than the free-ion value $B_0 = 1120$ cm^{-1}. Even so ^4P components are placed at 20 000–22 000 cm^{-1} only if ligand field splittings are also very large. Similarly an assignment of one of the bands in the 15 800–18 000-cm^{-1} region as a component of ^4F also requires large values for the various e_σ. In either case by "large" we consider, say, 5500 cm^{-1} for N and O donors and 4500 cm^{-1} for Cl/H_2O. Altogether we favor an assignment of all three features in the 15 800–18 000-cm^{-1} region as components of ^4P and we list our objections to alternative assignments as follows: (i) The large e_σ values required for these alternatives seem unreasonable by comparison with values obtained by other studies of cobalt(II) complexes.[1] The bond lengths[3,4] in the present complexes seem unexceptional and somewhat longer than those typical for octahedra and provide no rationale for unusually large ligand field effects. (ii) If only one component of ^4P were assumed to lie at energies greater than 20 000 cm^{-1}, there is no possibility of calculating two components of ^4F between 16 000 and 18 000 cm^{-1}. (iii) In that larger e_σ values might be associated with larger e_π values and their effects oppose each other, placing one component of ^4F at 15 800 cm^{-1} or above would require especially large e_σ values. (iv) Calculations placing all components of ^4P within the "charge-transfer tail" yield unacceptable agreement with the single-crystal magnetic properties. (v) The possibility of components of the ^4P lying both within the resolved region at 16 000–18 000 cm^{-1} and within the "charge-transfer" region at >20 000 cm^{-1} suggests two possibilities: (a) two bands within the "ct tail" and one at 18 000 cm^{-1} and (b) one band in the "ct tail" and one at 18 000 cm^{-1}. Calculations show that (a) is only approachable for large e_σ values but then the splitting pattern is incorrect. The correct pattern is achievable for, say, e_σ(N,O) ~ 3000–4000 cm^{-1} and $e_\sigma(Cl/H_2O)$ ~ 5000 cm^{-1} with fairly large e_π(Cl) values: such a parameter set does reproduce the overall splitting of ca. 3000 cm^{-1} required for the present proposition (v) and puts only one band in the "resolved region" but does not simultaneously split the ^4F sufficiently to assign the remaining bands in the 16 000–18 000-cm^{-1} region. Parameter values yielding the reverse splitting pattern (b) cannot reproduce the required overall ^4P splitting of 2000–3000 cm^{-1}. (vi) Finally, even with the possibilities considered in (v), fits to the magnetic properties, though better than in case iv, are still poor.

We conclude, therefore, that the complete spin-allowed d–d spectrum occurs at energies less than 20 000 cm^{-1} and that the single band at 15 800 cm^{-1} and the split band at ca. 18 000 cm^{-1} are all to be assigned as involving transitions to components of ^4P. Similar energies and splittings of the ^4P bands in $Co(py)_2Cl_2$ and $CoCl_2{\cdot}2H_2O$ have been established by Ferguson.[10] We now consider the *detailed* reproduction of these features together with a close fitting of the crystal paramagnetism.

The chloro and aquo axial ligands lie almost exactly on a common normal to the chelate plane and are presumed to enter into cylindrically symmetric π bonding with the cobalt atom. Within the d orbital basis of the present model, therefore, the idealized effective molecular symmetry is D_{5h}. Recognition of the inexact fivefold symmetry refines this idealization to the C_{2v} point group with Co–N1 as the principal rotation axis, a distortion reflected in the spectral features in Figure 1. The ^4P term seems to be split into an orbital singlet at 15 800 cm^{-1} and an orbital doublet at 18 000 cm^{-1} secondarily split by ca. 500 cm^{-1}, reflecting the lower point group and, no doubt, spin–orbit coupling. While it is possible that one, or more, of the features at ca. 18 000 cm^{-1} might reveal a spin-forbidden transition augmented by an intensity stealing process, we consider the absence of any compelling positive indication that such is the case commends a spectral assignment of the simplest kind. Accordingly, we seek a parameter set (or sets) which will reproduce an overall splitting of ca. 2200 cm^{-1} with a slightly split orbital doublet lying at higher energy. The achievement of both these conditions, plus good reproduction of the crystal paramagnetism, is surprisingly exacting. In particular, the central feature of any parameter set even approximately capable of reproducing the spectrum is that the ligand field parameters of the axial ligands be at least as great as of those in the pentagon plane. It is important at this stage that we discuss the problem of parameter correlation, so that we may be sure that our assertion of the "normality" of the axial bonds is not based upon a mathematical ambiguity.

The angular overlap model describes how each member of, here, the d orbital basis is shifted in energy by overlap with appropriate ligand orbitals. If different orbitals on different ligands can affect a given d orbital in the same way, parameters assigned to these various ligand orbitals can cease to be separable and, depending upon the extent of the "geometric confusion", will be correlated. The higher the molecular symmetry the more correlation of this sort may be expected and it is largely for this reason that we believe the aom is most useful in low-symmetry chromophores, and it is in just such situations that competing symmetry-based models yielding *Ds*, *Dt*, and the like lose their utility.[1] For the present discussion, we define a reference frame in which Z is perpendicular to the pentadentate ligand and X is oriented from the metal to the pyridine nitrogen, N1. Then by mutual interaction with d_{xz}, d_{yz} there exists the possibility of some correlation between e_π(axial) and e_π(N,O). Similarly, there may be interaction between $e_{\pi\perp}$(N) and $e_{\pi\perp}$(O). No interaction between e_π(axial) and $e_{\pi\parallel}$(N,O) is expected, but some might be between e_σ(N,O) and $e_{\pi\parallel}$(N,O) via the d_{xy} and $d_{x^2-y^2}$ orbitals. There may also be some confusion between $e_{\pi\parallel}$ for N1, N2, and O. In parentheses we observe that in low molecular symmetries, such correlations are minimized because of simultaneous conditions of constraint being imposed as a given ligand orbital interacts with several different d orbitals. In the present case, the most important conclusion, however, is that we expect rather little correlation between e_σ(axial) and any other e_σ parameter (certainly none with e_π because of nodes), any small correlation being associated with the torus of the d_{z^2} orbital. Altogether, therefore, our conclusions concerning the "normality" of the axial bonds should stand. We emphasize this point because of the obvious challenge to be made in view of the plethora of ligand field parameters employed in the present model: the essential feature, hardly surprising in view of the gross geometry of the complex, is that we have a good separation between ligand field parameters referring to in-plane and out-of-plane ligands even though some care may be required within the plane itself.

Table III. $[Co(DAPSC)Cl,H_2O]^+Cl^-\cdot 2H_2O$ Summary of Simultaneous Best Fits to Spectrum and Magnetism (All Energies in cm^{-1})

	N1	N2, 5	O1, 2	$(Cl + H_2O)$
e_σ	4500	3500	2500	4000
$e_{\pi\parallel}$	0	0	400	800
$e_{\pi\perp}$	200	1000	2000	

B 800 ζ 500 k 0.5

calcd eigenvalues	obsd spectral peaks
18 170	18 200 sh
17 770	17 770
15 940	15 800
11 260	
9 300	
4 420	
3 830	
2 150	
1 300	
0 (av over spin quartet)	

Table IV. $[Co(DAPSC)(H_2O)_2]^{2+}(NO_3)_2{}^{2-}\cdot H_2O$ Summary of Simultaneous Best Fits to Spectrum and Magnetism (All Energies in cm^{-1})

	N1	N2, 5	O1, 2	H_2O
e_σ	4500	3500	2500	4500
$e_{\pi\parallel}$	0	0	400	400
$e_{\pi\perp}$	200	1000	2000	

B 800 ζ 500 k 0.5

calcd eigenvalues	obsd spectral peaks
18 870	19 000 sh
18 430	18 500
15 900	15 900
12 080	
10 300	
4 440	
3 970	
2 180	
1 300	
0 (av over spin quartet)	

Ultimately, good fits to both spectrum and magnetism of the chloroaqua complex are obtained within the following parameter ranges: $e_\sigma(N1) = 4000–4500\ cm^{-1}$, $e_\sigma(N2) = 3500–4000\ cm^{-1}$, $e_\sigma(O) = 2500–3000\ cm^{-1}$, $e_\sigma(Cl/H_2O) = 4000\ cm^{-1}$, $e_{\pi\parallel}$ = all zero (though $e_{\pi\parallel}(O)$ ca. 400 cm^{-1} is possible), $e_{\pi\perp}(N1)$ between ±200 cm^{-1} though fixed here as +200 cm^{-1}, $e_{\pi\perp}(N2)$ ca. 1000 cm^{-1}, $e_{\pi\perp}(O) = 2000–2500\ cm^{-1}$, $e_\pi(Cl/H_2O) = 800–1200\ cm^{-1}$ representing the average of $e_\pi(Cl)$ and $e_\pi(H_2O)$; B ca. 800 cm^{-1}, ζ ca. 500 cm^{-1}, and k 0.4–0.6. Parameter values in these ranges reproduce the ^4P spectrum satisfactorily and give an average agreement with all three principal crystal susceptibilities, throughout the temperature range, of ca. 95%. In line with earlier comments about correlations, we observe that a somewhat reduced value for $e_{\pi\perp}(O)$) (by, say, 500 cm^{-1}) is possible but only if taken with an increased value of $e_\pi(Cl/H_2O)$. On the other hand, values of $e_\sigma(O)$ greater than ca. 3000 cm^{-1} are not acceptable, for then the overall ^4P splitting is calculated too small. Within the parameter space just defined we have selected one particular set with which to represent the quality of spectral and magnetic fit achieved as in Table III and Figure 3.

For the *diaqua complex*, Figure 1 shows a similar spectral pattern with peaks at 19 000 (sh), 18 500, and 15 900 cm^{-1} approximately. The crystal susceptibilities were measured as quite different from those of the chloroaqua complex, the two molecules crystallizing in different cells. However, we attempted to fit both sets of properties together, beginning with parameter values like those found for the chloroaqua complex, and similar conclusions emerge for most parameter values. However, the different spectrum, characterized by a splitting of ca. 1000 cm^{-1} more than in the chloroaqua molecule but with the lowest component at virtually the same energy, can only be reproduced by taking a smaller value for e_π(axial) in which $e_\pi(H_2O)$ is now 0–400 cm^{-1} compared with the average of $e_\pi(Cl)$ and $e_\pi(H_2O)$ of ca. 800–1200 cm^{-1}. This result reflects the relative π-donor properties of water and chlorine ligands. The magnetic properties of the diaqua complex are also better reproduced by the lower e_π(axial) value. In Table IV and Figure 4 we present a comparison of observed and calculated spectral and magnetic properties for a selected parameter set within that parameter space.

Table V. Molecular Susceptibilities[a] Calculated with the Parameter Sets Given in Tables III and IV

	$[Co(DAPSC)Cl,H_2O]^+Cl^-\cdot 2H_2O$			$[Co(DAPSC)(H_2O)_2]^{2+}(NO_3)_2{}^{2-}\cdot H_2O$		
T/K	K_1	K_2	K_3	K_1	K_2	K_3
300	85	87	54	85	86	53
240	108	110	65	107	108	63
180	145	148	80	144	147	78
120	222	228	102	221	226	100
70	387	402	126	385	398	123
20	1147	1235	190	1142	1215	192

[a] cgsu × 10^4.

Table VI. Orientations of the Principal Molecular Susceptibilities (deg)

	chloroaqua complex			diaqua complex		
	X	Y	Z	X	Y	Z
K_1	8.8	81.9	93.5	7.8	97.8	89.3
K_2	81.7	170.7	85.9	82.2	7.8	90.4
K_3	87.2	85.5	5.4	90.7	89.6	0.8

Table VII. Direction Cosines

	chloroaqua complex[4]			diaqua complex[3]		
	a	b	c'	a	b	c'
X	0.0334	0.9978	0.0580	−0.2832	−0.8213	0.4952
Y	0.8996	−0.0048	−0.4366	0.4288	−0.5703	−0.7007
Z	−0.4354	0.0668	−0.8978	0.8579	0.0139	0.5137

Molecular Susceptibilities

The penultimate stage in the calculation of the crystal susceptibilities χ, used to optimize parameter values by comparison with experiment, is the calculation of molecular susceptibilities K. Corresponding to the fits shown in Table III and IV and Figures 3 and 4 are the molecular susceptibilities given in Table V.

Despite their quite dissimilar crystal susceptibilities, the molecular susceptibilities of the two complexes are much alike, as one should expect. The molecular tensors are characterized by being approximately axial with the "unique" direction K_3 in each case lying within 5° of the perpendicular to the pentadentate plane. The small in-plane anisotropy is such that the principal susceptibilities K_1 and K_3 lie close to the idealized C_2 axis Co–N1. Thus the electronic symmetry as revealed by the simultaneous fitting of magnetic and spectral properties is, for both complexes, nearly pentagonal bipyramidal but with a small, subsidiary perturbation reflecting the lower, idealized point group C_{2v}.

The orientations of the principal molecular susceptibilities change by less than 0.5° over the temperature range 10–300 K and at 170 K are as shown in Table VI, where the molecular frames X, Y, and Z are defined approximately with Z perpendicular to the pentagonal plane and X parallel to Co–N1. The exact orientations of these reference frames with respect

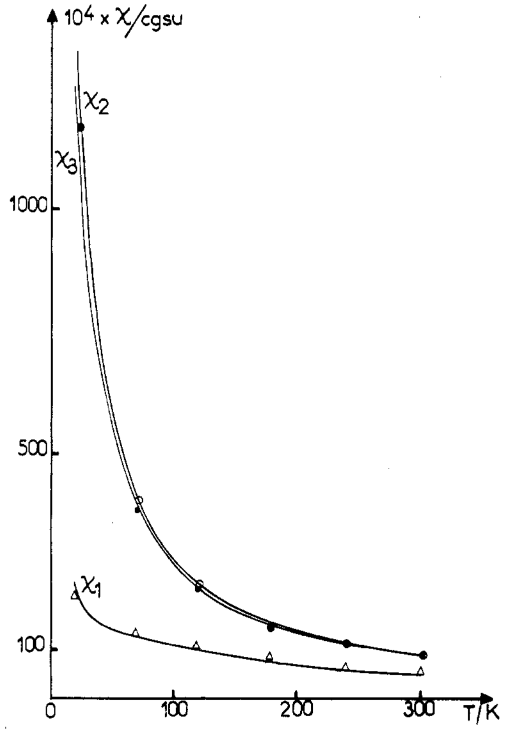

Figure 3. $[\mathrm{Co(DAPSC)Cl,H_2O}]^+\mathrm{Cl^-}\cdot 2\mathrm{H_2O}$. Comparison of principal crystal susceptibilities from experiment (full lines) and those calculated with parameters given in Table III. Calculated ϕ = 69°; observed $\phi \simeq 67°$.

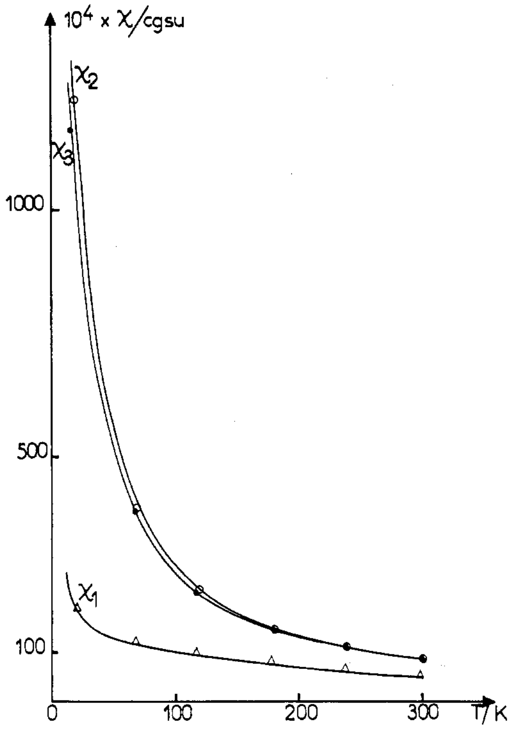

Figure 4. $[\mathrm{Co(DAPSC)(H_2O)}]^{2+}(\mathrm{NO_3^-})_2\cdot\mathrm{H_2O}$. Comparison of principal crystal susceptibilities from experiment (full lines) and those calculated with parameters given in Table IV. Calculated ϕ = 30°; observed $\phi \simeq 31°$.

to the appropriate orthogonalized unit cells have the direction cosines shown in Table VII.

Conclusions

We have applied the angular overlap model to the simultaneous quantitative interpretation of the spectra and single-crystal paramagnetic susceptibilities of two closely related seven-coordinate cobalt(II) complex ions. Despite misgivings with respect to the degree of parameterization required by this localized model in these difficult cases, the study appears to have been successful not only in faithfully reproducing all our experimental observations but also in doing so with ligand field parameters which make chemical sense in a way that symmetry based models with parameters like *Ds* and *Dt* do not. Interpretation of either property alone would not have been adequate to yield even qualitative conclusions.

The parameter sets for both complexes are virtually identical except that the replacement of one axial chlorine ligand by water is reflected in a lower π-bonding parameter for that ligand. The magnitude of the σ-bonding parameter for the axial ligands is sensibly in line with the observed bond lengths.[3,4] Thus in the chloroaqua complex, the Co–water bond length of 2.14 Å is similar, or slightly shorter, than the in-plane distances: a slightly lower position in the spectrochemical series for chlorine with respect to water might be expected so that $e_\sigma(\mathrm{Cl/H_2O})$, being the average for Cl and $\mathrm{H_2O}$, should be similar for the axial and equatorial ligands in these pentagonal-bipyramidal species, as observed. The values for $e_\sigma(\mathrm{N1})$ and $e_\sigma(\mathrm{N2,5})$ of 3500–4000 cm^{-1} are similar to values previously found[6,11,12] for pyridine and imine complexes of cobalt(II) and nickel(II). The same is true of the low $e_\pi(\mathrm{N1})$ value of the pyridine moiety and the larger $e_{\pi\perp}(\mathrm{N2})$ of the imine donor.[6,11]

The aom parameters found for the keto oxygen donor atoms in both the present complexes deserve further comment, however, in view of the "normality" of the Co–O bond lengths. The relatively low value (2500–3000 cm^{-1}) for the σ-bonding parameter of these donors seems sure, despite initial doubts about the efficacy of the aom to separately establish the various in-plane e_σ parameters: many attempts to reproduce the magnetic and spectral data with larger $e_\sigma(\mathrm{O})$ values than this, in various combinations with all other parameters, were unsuccessful. Values of e_σ obtained for various cobalt(II)–carboxylate interactions[13,14] are ca. 4000 cm^{-1} and for Ni(II)–phenolic oxygen[6,11] ca. 4000 cm^{-1}. It appears that the low $e_\sigma(\mathrm{O})$ value found here directly correlates with the lower base strength expected for keto groups compared with either phenolic or carboxylic ones, not least because of the charge on these latter groups: further the amide groups are expected to reduce the donor strength of the keto groups. The large positive $e_{\pi\perp}(\mathrm{O})$ observed presumably represents a strong π-donor capability of the $>\mathrm{C}{=}\!\!\rightarrow\Delta$ grouping, in a way complementary to the strong π-acceptor properties of $\Delta\!\leftarrow\!\mathrm{C}{=}\mathrm{O}$ in carbonyl complexes.

Finally it is entirely satisfactory that the molecular susceptibility tensor reflects the primary fivefold nature of the molecular geometry upon which is imposed a twofold distortion. We note that somewhat less good choices of the parameters, corresponding to discrepancies of say 500 cm^{-1} in the spectrum or of 10% in the magnetic fits, while maintaining the calculated K_3 perpendicular to the pentagon plane, invariably yielded K_1 and K_2 rotated by up to 40° from the idealized diad, Co–N1.

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Registry No. $[\mathrm{Co(DAPSC)(H_2O)_2}](\mathrm{NO_3})_2$, 71009-99-9; $[\mathrm{Co(DAPSC)Cl(H_2O)}]\mathrm{Cl}$, 71048-86-7.

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Magnetic and Spectral Properties of Chloroaqua[2,6-diacetylpyridine bis(semicarbazone)]iron(II) and Diaqua[2,6-diacetylpyridine bis(semicarbazone)]nickel(II): Ligand Fields and Bonding in Pentagonal-Bipyramidal Complexes

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Principal crystal susceptibilities throughout the temperature range 10–300 K have been measured for the complexes $[Ni(DAPSC)(H_2O)_2]^{2+}(NO_3^-)_2\cdot H_2O$ and $[Fe(DAPSC)Cl,H_2O]^+Cl^-\cdot 2H_2O$, where DAPSC is 2,6-diacetylpyridine bis(semicarbazone). The unpolarized, single-crystal transmission spectra have been recorded in the UV, visible, and near-IR regions. The complete crystal magnetic properties and spectral features of the nickel complex have been reproduced simultaneously within the angular overlap model (aom) the parameters of which reflect the longer Ni–O(keto) bond lengths observed relative to Co–O in the analogous cobalt complex. The magnetism of the iron system is quantitatively reproduced by a similar model and reflects the similarity of the Fe–O(keto) bond lengths with respect to those in the cobalt complex. A detailed discussion of the equivalent orbital diagrams established by the ligand field analyses of the iron(II), cobalt(II), and nickel(II) complexes is presented, from which a rationale of the first-coordination-shell bond lengths in these and the analogous copper(II) molecules emerges.

Introduction

In the preceding paper[1] we reported a study of the spectral and single-crystal magnetic properties of two formally pentagonal-bipyramidal cobalt(II) complexes involving the 2,6-diacetylpyridine bis(semicarbazone) ligand (DAPSC). The results were interpreted within an angular overlap model (aom), parameters referring to the local σ- and π-bonding interactions between the central metal atom and each ligand. We present here a study of the spectral and single-crystal magnetic properties of two other members of this series in order to complement discussions by Palenik and Wester[2-5] upon trends revealed by their X-ray structural analyses of these species. The complexes studied here are $[Fe(DAPSC)Cl,H_2O]^+Cl^-\cdot 2H_2O$ and $[Ni(DAPSC)(H_2O)_2]^{2+}(NO_3^-)_2\cdot H_2O$. Again the efficacy of the angular overlap model and of our application of it to the magnetic and spectral properties of low-symmetry molecules[6] is of particular interest and we show that not only are the experimental magnetism and spectroscopy quantitatively reproduced by the technique but also they are reproduced in a manner which directly relates to the bonding and structure in this series of complexes.

Experimental Section

The 2,6-diacetylpyridine bis(semicarbazone) ligand (DAPSC) was prepared as described previously.[1] The complex of stoichiometry DAPSC, $FeCl_2$, $3H_2O$ was prepared in a manner similar to that[1] of the cobalt analogue, from iron(II) chloride, except that crystallization of the complex $[Fe(DAPSC)Cl,H_2O]^+Cl^-\cdot 2H_2O$ took place directly from the concentrated solution without previous dissolution in water. The solution is somewhat unstable with respect to air and water but yields black platelike crystals which are stable to the atmosphere. Satisfactory C, N, H, and Cl analyses are reported in Table I.

Crystals of the nickel complex DAPSC, $Ni(NO_3)_2$, $3H_2O$ were prepared as for the analogous cobalt compound. However, two different crystal forms are produced: one, yellow-green, was found to have the unit cell dimensions listed by Palenik[2] for the desired complex; the other, forming green rods, was found to crystallize in a triclinic cell with dimensions $a = 7.04$ Å, $b = 12.49$ Å, $c = 13.44$ Å, $\alpha = 119.5°$, $\beta = 107.2°$, and $\gamma = 75.89°$. The cocrystallization of the two forms, while in no way preventing our obtaining good crystals of the desired crystals, is undoubtedly responsible for the less good analyses reported in Table I. That the analytical figures are nevertheless fair suggests that the stoichiometry of the triclinic form is similar to that of the monoclinic one. Further study of the triclinic crystals is currently under way.

Susceptibility measurements of the iron and nickel monoclinic crystals, isomorphous with the corresponding cobalt complexes, were performed throughout the temperature range 10–300 K, as described previously.[1] Duplicate measurements from different crystals agree to better than 3%. Values for the monoclinic ϕ angles, calculated from the equation[7]

$$\sin^2 (\beta - 90° - \phi) = (\chi_{a'} - \chi_1)/(\chi_2 - \chi_1)$$

were determined as −25 and −55 °C for the iron and nickel crystals, respectively.

After the correction for a gross diamagnetic susceptibility of -170×10^{-6} cgsu, determined for the DAPSC, $ZnCl_2$, $3H_2O$ complex, the interpolated, principal crystal susceptibilities of the two complexes are collected in Table II.

The electronic absorption transmission spectra have been recorded for crystals of the pure nickel complex and for crystals of the zinc complex doped with ca. 10% iron. The spectrum of the nickel compound, recorded at ca. 80 K by using a Cary 14 spectrometer, is reproduced in Figure 1. No significant spectral features have been observed for the iron complex apart from the onset of a charge-transfer region above 20 000 cm^{-1}.

Discussion

A. Fitting Spectral and Magnetic Properties. Using the same techniques as in the earlier paper[1] and as reported in detail elsewhere,[8] we performed calculations of eigenvalues, eigenvectors, and magnetic properties within the complete

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