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A Re-interpretation of the Recorded Electronic Spectrum and Crystal Structure of Bis[2-(2-aminoethyl)aminoethanol]nickel(II) Nitrate using the ULFM and Calculated Racah Parameters

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Abstract

The electronic spectrum of the bis[2-(2-aminoethyl)aminoethanol]nickel(II) nitrate complex was measured. An X-ray analysis revealed a C_1 symmetry. Application of the Unified Ligand Field Model and calculation of the Racah parameter B explained the similarity between the observed spectrum and those of octahedral high-spin Ni(II) complexes, and resulted in adjustments to the assignment of the spectrum. Effective ligand charges were calculated and explained. The symmetry, electronic spectrum and B value for bis(2,2′-oxybisethanamine)nickel(II) nitrate were anticipated.

Introduction

In the study of a metal–ligand complex, it is of interest to simulate the observed electronic spectrum. One way in which one can attempt to do this is to use the Unified Ligand Field Model (ULFM) previously described [1]. This model has already been used successfully on d^1 and d^9 systems [2, 3]. In this work the ULFM was applied to the interpretation of the electronic spectrum of the bis[2-(2-aminoethyl)aminoethanol]nickel(II) nitrate complex. This complex differs in two respects from the substances previously studied by this method: it is a d^8 system and a chelate complex.

As is well known, chelate complexes show enhanced stability over complexes of monodentate ligands having the same donor atoms; this enhanced stability is termed the 'chelate effect' [4].

The coordinating properties of the ligand 2-(2-aminoethyl)aminoethanol (hereafter referred to as etolen) in the above-mentioned complex have been the subject of some discussion in the literature [5–16]. There has been some controversy as to whether etolen coordinates as a bi- or a tri-dentate ligand. To clarify this point the crystal structure of the bis(etolen)Ni(II) nitrate complex was determined. The crystallographic data were also required for the theoretical calculations.

The interpretation of the electronic spectrum of another d^8 chelate complex was attempted, namely that of bis(2,2′-oxybisethanamine)nickel(II) nitrate. It was found to be extremely difficult to obtain crystals of crystallographic quality of the $[Ni(oden)_2](NO_3)_2$ complex. Hence the lack of the required crystallographic data hampered adequate investigation of this complex.

Experimental

Preparation of $[Ni(etolen)_2](NO_3)_2$

A quantity of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in the minimum amount of hot ethanol. This solution was then added dropwise to a sample of neat etolen. The molar ratio of the metal salt to the ligand was 1:2. An equal volume of acetone containing 10% butanol was then added to the mixture. On cooling the mixture in ice, crystals were obtained.

The space group and approximate cell constants were determined by standard oscillation and Weissenberg techniques using Co Kα radiation.

The blue crystals were found to be suitable for an X-ray structural study and this was done by Wade [17].

Electronic Spectrum

A solution containing a metal-to-ligand ratio of 1:2 was prepared. The spectrum of this solution was recorded on a Pye Unicam SP 1800 UV–Vis spectrophotometer. This instrument scans up to 710 nm (14 kK) only. The resulting spectrum is shown in Fig. 1.

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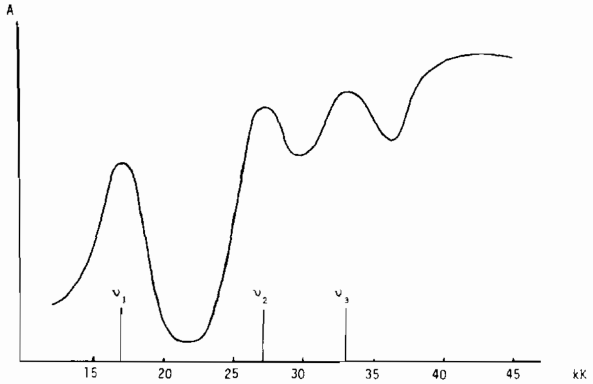

Fig. 1. Absorption spectrum of $[Ni(etolen)_2]^{2+}$ (absorbance in arbitrary scale).

Theoretical

The measured spectrum of $[Ni(etolen)_2]^{2+}$ displayed in Fig. 1. resembles those of the six-coordinated Ni(II) high-spin d^8 configurations, as discussed by various authors [18–20] – in contrast to the spectra of the corresponding low-spin systems. In the high-spin complexes studied by König [20], however, the observed peaks fall within the range 7–23 kK. This merits further investigation.

The X-ray analysis of the crystal structure revealed a triclinic space group having a C_1 microsymmetry (Fig. 2). For such a low-symmetry complex, group theoretical considerations, based on the dimensionality of the irreducible representations, predict only non-degenerate energy levels [21] – in contrast to the presence of degenerate levels implied in the six-coordinated Ni-complexes discussed by Jϕrgensen and König [18–20].

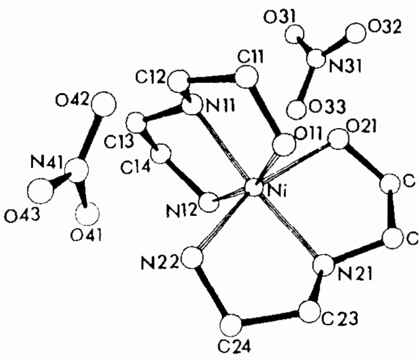

Fig. 2. Crystal structure of $[Ni(etolen)_2]^{2+}$ (reproduced from Ref. 17). Bond lengths (Å): Ni–O11, 2.162; Ni–N11, 2.049; Ni–N12, 2.08; Ni–O21, 2.136; Ni–N21, 2.064; Ni–N22, 2.121. Angles (°): O11–Ni–N11, 80.8; O11–Ni–N12, 163.0; N11–Ni–N12, 82.3; O11–Ni–O21, 88.7; O11–Ni–N21, 95.7; O11–Ni–N22, 85.0; N11–Ni–N22, 100.1; N12–Ni–N22, 96.5; O21–Ni–N21, 80.4; O21–Ni–N22, 161.5; N21–Ni–N22, 83.0; O21–Ni–N11, 96.0; O21–Ni–N12, 94.6; N21–Ni–N12, 101.3.

The availability of crystallographic data and a tentative spectrum for $[Ni(etolen)_2]^{2+}$ facilitates the application of the ULFM to this complex, in order to assign the observed transitions and perhaps obtain a clearer perception of the effective symmetry and other properties of this molecule.

The ULFM expresses the influence of covalence in terms of parameters reminiscent of the Angular Overlap Model (AOM), whereas the ionic contributions are described by means of a reparameterization of the Point Charge Electrostatic Model (PCEM). In the case of d-orbitals the destabilization energy of orbital $|M_i>$ due to N identical ligands can then be expressed as eqn. (1):

$$E_{m_i} = \sum_{L}^{N}\sum_{m}^{5} (A_{im}{}^{L})^2 e_m + \sum_{L}^{N}\sum_{m}^{5} (A_{im}{}^{L})^2 U_m \qquad (1)$$

The $A_{im}{}^{L}$ are elements of the unitary matrix which defines the transformation of the central ion orbitals $|M_i>$, expressed in the molecular coordinate system XYZ, to those expressed relative to a diatomic coordinate system $X'Y'Z'$ defined such that ligand L is on the positive Z'-axis. Hence $A_{im}{}^{L}$ is a function of the angular position of ligand L.

The AOM parameters e_m are given by

$$e_m = [(\tfrac{1}{4}H_l^2 + \tfrac{1}{2}H_m H_l - \tfrac{3}{4}H_m{}^2)/(H_m - H_l)]\, S_{ml}{}^2$$

where $H_m = \langle M_i | H | M_i \rangle$ and $H_l = \langle X_j | H | X_j \rangle$ are associated with the VOIEs of the relevant metal and ligand orbitals $|M_j>$ and $|X_j>$. S_{ml} is the appropriate diatomic overlap.

When the symmetry-orientated electrostatic parameters U_m are expressed in terms of the radial parameters

$$\alpha_K^L = Z_L e^2 \int_{r=0}^{\infty} (R_{nl})^2 \frac{r_<^k}{r_>^{k+1}} r^2 \, dr$$

one obtains for d-orbitals [22]

$$\begin{array}{lll} d_{z^2} & U_1 = \alpha_0 + \frac{2}{7}\alpha_2 + \frac{2}{7}\alpha_4 & \\ d_{yz}, d_{zx} & U_2 = U_3 = \alpha_0 + \frac{1}{7}\alpha_2 - \frac{4}{21}\alpha_4 & (2) \\ d_{xy}, d_{x^2-y^2} & U_4 = U_5 = \alpha_0 - \frac{2}{7}\alpha_2 + \frac{1}{21}\alpha_4 & \end{array}$$

Systems with different ligands and/or metal–ligand distances involve the introduction of additional parameters e'_m, U'_m etc., as will be illustrated.

Axes should be chosen such that the z-axis is in the Ni–N_{11} direction and N_{22} in the xz-plane. Equation (1) and the angles given in Fig. 2 then result in the following d-orbital energies:

$$E_{d_{z^2}} = 2.42[e_1 + U_1] + 0.45[e'_1 + U'_1] + 0.16[e_3 + U_3] + 0.11[e'_3 + U'_1] + 1.44[e_5 + U_5] + 1.44[e'_5 + U'_5]$$

$$E_{d_{yz}} = 0.05[e_1 + U_1] + 0.075[e'_1 + U'_1] + 2.96[e_3 + U_3] + 0.91[e'_3 + U'_3] + 1.0[e_5 + U_5] + 1.09[e'_5 + U'_5]$$

$$E_{d_{zx}} = 0.11[e_1 + U_1] + 0.03[e'_1 + U'_1] + 2.88[e_3 + U_3] + 0.99[e'_3 + U'_3] + 1.01[e_5 + U_5] + 0.99[e'_5 + U'_5]$$

$$E_{d_{xy}} = 0.004[e_1 + U_1] + 0.05[e'_1 + U'_1] + 1.96[e_3 + U_3] + 1.9[e'_3 + U'_3] + 2.05[e_5 + U_5] + 0.17[e'_5 + U'_5]$$

$$E_{d_{x^2-y^2}} = 1.43[e_1 + U_1] + 1.39[e'_1 + U'_1] + 0.05[e_3 + U_3] + 0.11[e'_3 + U'_3] + 2.52[e_5 + U_5] + 0.5[e'_5 + U'_5]$$

In these expressions the primed and unprimed parameters refer to the Ni–O and Ni–N bonds respectively. The accuracy of these results may be checked by using the sum rule [22]

$$\sum_{L}^{N} \sum_{j}^{2l+1} (A_{ij}{}^{L})^2 = \sum_{N}^{L} \sum_{j}^{2l+1} (A_{ji}{}^{L})^2 = N$$

which implies that in each energy the sum of the coefficients of the terms like $[e_i + U_i]$ must equal $N = 6$.

These equations show that the one-electron energies for this complex, having C_1 symmetry, are nondegenerate, as anticipated. The spectrum associated with the one-electron transitions is, however, reminiscent of an approximately O_h symmetry, implying equal ligands at equal distances from the central ion. Since the actual distances are very similar and both the oxygen and nitrogen ligands entering the bonding are neutral, it is feasible that the charges deposited on them as a result of the complex formation may be comparable. Assuming this to be the case and considering only electrostatic effects one finds (after replacing the U values by the α values as in eqn. 2 that

$$E_{d_{z^2}} = 6\alpha_0 + 0.03\alpha_2 + 0.91\alpha_4$$

$$E_{d_{x^2-y^2}} = 6\alpha_0 - 0.03\alpha_2 + 0.91\alpha_4$$

$$E_{d_{xy}} = 6\alpha_0 - 0.06\alpha_2 + 0.61\alpha_4$$

$$E_{d_{yz}} = 6\alpha_0 - 0.01\alpha_2 - 0.6\alpha_4$$

$$E_{d_{zx}} = 6\alpha_0 + 0.02\alpha_2 - 0.6\alpha_4$$

Since $E_{d_{z^2}} \simeq E_{d_{x^2-y^2}}$ and $E_{d_{xy}} \simeq E_{d_{yz}} \simeq E_{d_{zx}}$, the above calculations offer an explanation for the O_h-like spectrum of $[\mathrm{Ni(etolen)_2}]^{2+}$. It is also clear that the measured angular deviation from a perfect O_h symmetry is not sufficient to result in a spectrum appreciably different from those observed for octahedral high spin Ni(II) complexes.

It is therefore appropriate to regard $[\mathrm{Ni(etolen)_2}]^{2+}$ as having O_h symmetry. The high energy range, 17–33 kK, needs to be investigated, however.

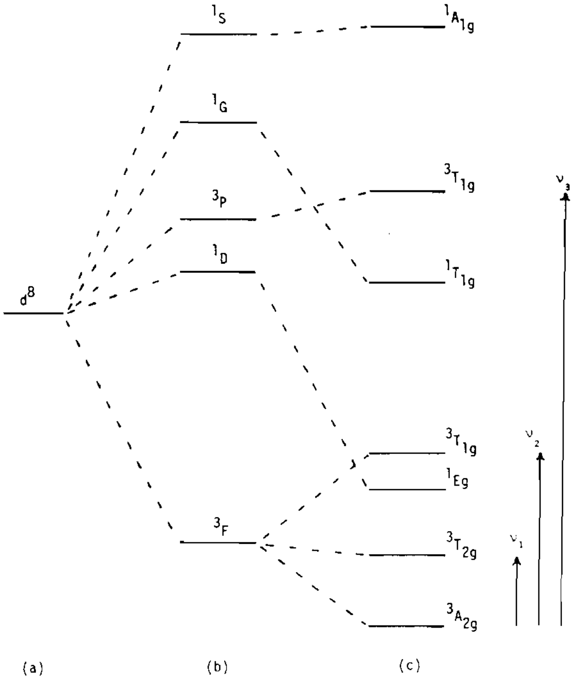

Fig. 3. Energy level diagram of a d^8 electronic configuration: (a) unperturbed system; (b) effect of interelectronic interaction; (c) effect of an octahedral field.

The ground state of the free ion, having a d^8 configuration, is ^{3}F [23]. In an octahedral environment this d^8 ground state term (as well as the other terms) splits up as indicated in Fig. 3 [24, 25]. In both the strong and weak field cases a $^3A_{2g}$ ground state results [26].

In the presence of a centre of symmetry, transitions between states originating from the same term would be parity-forbidden. However, since we are concerned with an at best distorted O_h symmetry, such transitions are allowed in the present complex.

The three spin-allowed transitions involving the ground state are $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, to which we assign the energies ν_1 = 17.5 kK, ν_2 = 27.7 kK and ν_3 = 33.0 kK, respectively [18–20].

If one compares this with the spectra of other octahedral Ni(II) complexes the above-mentioned discrepancy becomes evident. For $[Ni(H_2O)_6]^{2+}$ $\nu_1 = 8.5$ kK, $\nu_2 = 13.5$ kK and $\nu_3 = 25.3$ kK, whereas for $[Ni(NH_3)_6]^{2+}$ $\nu_1 = 10.7$ kK, $\nu_2 = 17.5$ kK and $\nu_3 = 28.2$ kK [25]. Similarly, for the numerous approximately octahedral Ni(II) complexes tabled by König [20] the range $\nu_1 \rightarrow \nu_3$ is 7–29 kK, i.e., well below ours.

König derived formulae for calculating the interelectronic repulsion parameter B from the observed transition energies ν_1, ν_2 and ν_3. Depending upon the availability of the various transitions the following formulae were obtained as applicable to octahedral d^8 systems:

(a) $B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1)$

(b) $B = (2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1)$

(c) $B = (\nu_2 + \nu_3 - 3\nu_1)/15$

(d) $B = \frac{1}{75}[3\nu_1 \pm \{25(\nu_3 - \nu_2)^2 - 16\nu_1^2\}^{1/2}]$

(e) $B = (\nu_2 + \nu_3 - 30\,Dq)/15$.

Using our assignment of the observed peaks in $[Ni(etolen)_2]^{2+}$, one obtains from these formulae the following values, respectively: (a) $B = 1290$ cm^{-1}; (b) $B = -1501$ cm^{-1}; (c) $B = 539$ cm^{-1}; (d) B becomes complex; and (e) $B = 1709$ cm^{-1}.

According to the values tabled by König for octahedral Ni(II) complexes, B lies in the range 800–1350 cm^{-1}. Furthermore, König concludes that the best fit of calculated energies, as compared with observed ones, is obtained when the value of B calculated from (c) is used in calculating the energies from the formulae

$$\nu_1 = 10Dq$$

$$\nu_2 = \tfrac{1}{2}(15B + 30Dq) - \tfrac{1}{2}[(15B - 10\,Dq)^2 + 12B \cdot 10Dq]^{1/2}$$

$$\nu_3 = \tfrac{1}{2}(15B + 30Dq) + \tfrac{1}{2}[(15B - 10\,Dq)^2 + 12B \cdot 10Dq]^{1/2}$$

In the present study B, as obtained from (c), is 539 cm^{-1} and $10Dq = 17.5$ kK. Hence the calculated transitional energies become $\nu_2 = 23.2$ kK and $\nu_3 = 37.5$ kK. If $B = 1290$ cm^{-1} (which lies within the acceptable range) is used instead, one obtains $\nu_2 = 27.4$ kK and $\nu_3 = 44.0$ kK.

These results, based on the present assignment of the observed spectrum, are unsatisfactory and one is inclined to conclude that our interpretation of the spectrum should be questioned. Furthermore, Hancock *et al.* [27] proposed a value of 870 cm^{-1} for the Racah parameter B.

In view of the above comparisons between the present spectrum of $[Ni(etolen)_2]^{2+}$ and those of typical octahedral Ni(II) complexes, it is concluded that the lowest peak has actually not been measured. Henceforth the $10Dq$ value of 10.9 kK proposed by Hancock and Thöm [27] will be taken as ν_1. Hence $\nu_2 = 17.5$ kK and $\nu_3 = 27.7$ kK.

Using these three transition energies in formulae (c) and (d) gives $B = 833$ cm^{-1} and $B = 789$ cm^{-1} respectively.

The energies calculated with $B = 833$ cm^{-1} are then $\nu_2 = 17.3$ kK and $\nu_3 = 27.9$ kK. With $B = 789$ cm^{-1} these become $\nu_2 = 17.2$ kK and $\nu_3 = 27.4$ kK. Using the measured value of $B = 870$ obtained by Hancock and Thöm [27] one obtains $\nu_2 = 17.4$ kK and $\nu_3 = 28.3$ kK.

From the above it is clear that (c) gives a better fit than (d) – in accordance with the findings of König. Furthermore the corresponding value of $B = 833$ cm^{-1} falls within the range observed for Ni(II) complexes. It also gives a slightly better energy fit than Hancock's value.

In view of the foregoing conclusions it is realistic to use the new assignments as proposed in any further investigations. Furthermore, we have sufficient evidence suggesting that the present complex is of a typical O_h symmetry.

An estimate of the effective charges in the ligands can be obtained from an application of the ULFM to the value for $10Dq = \nu_1$, which corresponds to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition. Here the ground state configuration is $t_{2g}{}^6\ e_g{}^2$ and that of the excited state $t_{2g}{}^5\ e_g{}^3$ [25]. Hence, in terms of the relevant one-electron energies in an O_h environment, one gets

$$\begin{aligned}10Dq = E_{e_g} - E_{t_{2g}} &= 3(e_1 + U_1) - 4(e_3 + U_3) \\ &\quad + (e_5 + U_5) \\ &= 3e_1 - 4e_3 + e_5 + \tfrac{5}{3}\alpha_4\end{aligned}$$

Using the average metal–ligand distance of 2.1 Å in conjunction with Ballhausen and Ancmon's tables [28] one ultimately finds $\alpha_4 = 28.48Z$, Z being the ligand charge. When covalence is ignored one finally obtains $10Dq = 47.47Z = 10.9$ kK. Hence $Z = 0.23$, implying an average negative charge of 0.23 electrons on each ligand. If σ bonding is included in the way illustrated elsewhere [2, 3], the above value does not change appreciably. This is due to the small covalence parameter ($e_1 = 0.3$ kK) resulting from the particular metal–ligand distances appropriate to this complex [29].

Conclusions

$[Ni(etolen)_2]^{2+}$ is a further example of the many Ni(II) complexes having actually a distorted octahedral symmetry, but for which no splittings lower than O_h symmetry are observed [20]. The proximity of this complex to an O_h arrangement was quantitatively illustrated by using the ULFM.

The average ligand charge of 0.23 electrons, as calculated from the electrostatic contributions to the ULFM, cannot be due to a metal–ligand charge transfer, as that would even further increase the positive charge on Ni(II). Since oxygen and nitrogen are more electronegative than carbon, it is feasible to attribute the electron gain of the ligands as originating from the carbon atoms in CH_2.

The depositioning of a total of 1.4 electrons on the initially neutral ligands, resulting in a reduced overall charge by offsetting the positive charge on Ni(II), is in accordance with the electroneutrality principle and enhances stability, as expected in a chelate complex due to the inductive effect of the chelate bridges. Stability is further increased by the octahedral symmetry, this being the most stable arrangement for Ni(II) high-spin complexes, according to Valach *et al.* [30].

The calculation of the Racah parameter using König's formulae, as well as his extensive tables, were essential elements in deciding on the final assignment of levels for this complex. Only after the correct assignment was introduced did it become possible to place $[Ni(etolen)_2]^{2+}$ where it belongs: amongst the stable octahedral high-spin Ni(II) complexes.

In the case of $Ni[(oden)_2]^{2+}$, no crystal structure is available. Furthermore the measured spectrum exhibits peak at 17.1, 27.3 and 33.1 kK. In this case we assume octahedral symmetry and take the first two energies to represent ν_2 and ν_3 respectively. Then ν_1 is calculated [20] using $\nu_1 = 10Dq = \frac{1}{34}[9(\nu_2 + \nu_3) \pm \{81(\nu_2^2 + \nu_3^2) - 178\nu_2\nu_3\}^{1/2}]$, which gives $\nu_1 = 10.8$ kK or $\nu_1 = 12.6$ kK. Utilizing $B = (\nu_2 + \nu_3 - 3\nu_1)/15$ for each case gives $B = 783$ cm^{-1} and $B = 439$ cm^{-1} respectively. Only the former falls in the range typical of O_h Ni(II) complexes and hence it is anticipated that $Ni[(oden)_2]^{2+}$ has an O_h symmetry with electronic transition energies $\nu_1 = 10.8$ kK, $\nu_2 = 17.1$ kK and $\nu_3 = 27.3$ kK.

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