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Electron Paramagnetic Resonance Spectra of Molybdenum(III) Complexes: Direct Observation of ^{95}Mo Hyperfine Interaction and Implications for Molybdoenzymes

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A series of complexes of Mo(III) has been examined by low-temperature EPR spectroscopy. Mononuclear six-coordinate Mo(III) complexes with Cl, N, O, or S ligands show broad axial or rhombic signals centered at $g = 2$ and 4, attributable to the $\pm^1/_2$ Kramers' doublet of an $S = {}^3/_2$ system with large zero-field splitting. Substitution of ^{95}Mo results in readily observable broadening of these signals and, in the case of Mo(acac)$_3$, splitting of the g_z portion of the signal due to the $\pm^3/_2$ Kramer's doublet. A value of $A_\perp$ of 10 ± 1 mK is estimated for the $\pm^1/_2$ doublet of Mo(acac)$_3$, while a value of A_z of 12.2 ± 0.5 mK is observed for the $\pm^3/_2$ doublet. The temperature dependence of the signals establishes that $D <$ 0 for Mo(acac)$_3$. Complexes with unsaturated sulfur ligands (diethyldithiocarbamate, *o*-aminothiophenol, and 8-mercaptoquinoline) show atypical EPR spectra, with all g values near 2.

Molybdenum is known to be an essential constituent of a number of enzymes that catalyze oxidation–reduction reactions, including nitrogenase and nitrate reductase.[2] One of the major physical techniques used to study these enzymes has been electron paramagnetic resonance (EPR) spectroscopy, since both Mo(V) and Mo(III) are expected to be paramagnetic and thus potentially observable by EPR spectroscopy. Although Mo(V) in a number of enzymes, most notably xanthine oxidase,[3] has been extensively studied by EPR spectroscopy, the presence of Mo(III) has only been proposed, but not confirmed, for bacterial nitrate reductase,[4] and remains a possibility in nitrogenase. This state of affairs is due at least in part to conflicting reports in the literature as to the EPR properties of simple Mo(III) complexes. Thus, the axial signals observed near $g = 2$ for nitrate reductase at 80–100 K by Forget and DerVartanian[4] are quite similar to those reported by Mitchell and Scarle[5] for a series of complexes of Mo(III) with sulfur-containing ligands. In contrast, the rhombic signal ($g = 4.3, 3.7, 2.0$) of the Mo–Fe protein of nitrogenase,[6] observable only at ≤20 K, and a similar signal observed in reduced samples of nitrate reductase from *Neurospora crassa*[2b,7] are analogous to that reported for molybdenum(III) acetylacetonate, Mo(acac)$_3$, in an Al(acac)$_3$ matrix.[8]

Since all known molybdenum enzymes contain additional cofactors (heme, flavin, Fe–S) that are also potentially EPR active, it is essential to be able to unambiguously assign a given resonance to molybdenum. In principle, substitution of ^{95}Mo ($I = {}^5/_2$) should split a given resonance into six lines provided that the line widths are much less than the hyperfine coupling constant, $A(^{95}\text{Mo})$, or at least broaden the signal if the line width is comparable to $A(^{95}\text{Mo})$. The molybdenum-containing oxidases examined to date all show, under appropriate conditions, narrow resonances analogous to those of mononuclear Mo(V) complexes, with $\langle g \rangle \sim 2.0$ and $\langle A \rangle$ of 30–70 G.[2a] In contrast, no ^{95}Mo hyperfine was observed for Mo(acac)$_3$ containing natural abundance molybdenum[8] or for the Mo–Fe protein of nitrogenase enriched in ^{95}Mo.[2b,9] We have therefore examined the EPR spectra of a series of Mo(III) complexes, in order to ascertain the general properties of such signals (g values, line width, temperature dependence, and ^{95}Mo hyperfine coupling constants).

Experimental Section

All samples were prepared in an atmosphere of argon purified to contain ≤1 ppm oxygen,[10] by using the double septum seal (dss) apparatus described previously,[11] unless indicated otherwise. Ammonium diethyl dithiophosphate, 8-hydroxyquinoline, sodium diethyldithiocarbamate, and 2,4-pentanedione were commercial reagents. 2-Aminothiophenol was purified by vacuum distillation. Commercial 8-mercaptoquinoline hydrochloride was purified by reaction with sodium hypophosphite in hydrochloric acid[12] and isolated as the crystalline red dihydrate. The complexes $(NH_4)_2[MoCl_5(H_2O)]$ and $(NH_4)_3[MoCl_6]$ were prepared by electrolysis of HCl solutions of MoO_3[13] and isolated as described by Brencic and Cotton.[14] Isotopically enriched $(NH_4)_3[^{95}MoCl_6]$ was prepared by an analogous route: 30 mg of ^{95}Mo metal (~97% ^{95}Mo) was dissolved in 8 mL of aqua regia, the solution evaporated to dryness on a hot plate several times with 12 N HCl, and the resulting pale yellow solution electrolyzed. Aluminum acetylacetonate was prepared by a published method.[15] EPR spectra were recorded on a Varian 109 spectrometer operating at X-band with 100 kHz modulation; sample temperature was varied over the range 5–80 K by using boiloff gas from liquid helium as the coolant.

Because of the limited amount of isotopically enriched material available and the *extreme* oxygen sensitivity of Mo(III) complexes with O, N, and S ligands, the following method for generating complexes from the air-stable $(NH_4)_3[MoCl_6]$ was adopted. To 1.64 mg (5 μmol) of $(NH_4)_3[MoCl_6]$ in a dss tonometer was added 1.25 mL of an approximately 1 M solution of the ligand in distilled water. The resulting solution was stirred vigorously until all the starting material had dissolved and a dark precipitate of the desired tris chelate had formed. Toluene (0.50 mL) was then added, the mixture stirred until the solid had dissolved, and the resulting mixture of two phases transferred via gastight Hamilton syringe to a dss semimicrocuvette (10 × 4 mm). After the two phases had separated, an aliquot (50 or 100 μL) of the upper layer was removed via syringe and diluted to 500 μL with toluene in a dss tonometer attached to an EPR tube.

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Table I. EPR Spectra Parameters of Complexes Examined

complex	color	apparent g values
$Mo(acac)_3$	red	4.11, 3.35, 1.95
$MoCl_6^{3-} + S_2P(OEt)_2^-$	orange-red	4.58, 2.67, 1.92
$MoCl_6^{3-}$ [a]	salmon	5.37, *b*, 1.83
$MoCl_5(H_2O)^{2-}$ [c]	orange-red	5.22, *b*, 1.88
$MoCl_6^{3-}$ + 8-OH-quin	green	5.51, *b*, *d*
$MoCl_6^{3-} + Et_2dtc^-$	orange-red	2.02, 1.98[e] 1.98[f]
$MoCl_6^{3-} + o\text{-}H_2NC_6H_4SH$	brown	2.00
$MoCl_6^{3-}$ + 8-SH-quin	brown	2.29, 2.17, 1.97

[a] Solvent: 12 N HCl. [b] Exact position not well-defined due to width of lines and pronounced rhombicity of spectrum. [c] Solvent: 6 N HCl. [d] Position obscured by Mo(V) impurity. [e] Low power (10 μW) spectrum; $g_{av} = 1.989$. [f] High power (30 mW) spectrum.

After being mixed thoroughly, the solution was transferred to the EPR tube and rapidly frozen (isopentane slush). In the case of 8-mercaptoquinoline, 8-hydroxyquinoline, and 2-aminothiophenol (which are insoluble in water), the ligands were dissolved in *N,N*-dimethylacetamide and 0.60 mL of the ligand solution was added to the solid $(NH_4)_3[MoCl_6]$, followed by 0.75 mL of H_2O and 0.50 mL of toluene. Both 8-mercaptoquinoline and 2-aminothiophenol gave products which did not dissolve totally under these conditions; the spectra described were thus obtained on the toluene supernatant.

Results and Discussion

The method for preparation of samples was designed to take advantage of the relatively high solubility of neutral metal tris chelates in organic solvents and allow minimal handling of milligram amounts of highly oxygen-sensitive, often pyrophoric materials. Thus, reaction of hexachloromolybdate(III) with monoprotic ligands in water or mixed aqueous–organic solvents affords good yields[16] of complexes such as[17] $Mo(acac)_3$; direct extraction into a nonpolar solvent such as toluene leaves charged complexes, including starting material and possible byproducts, in the aqueous layer. Since the complexes to be examined by EPR spectroscopy were not isolated in pure form, it is reassuring to note that in most cases the products obtained via the indicated procedure have properties which are consistent with earlier work. Small and variable amounts of coextracted Mo(V) complexes were observed in the $g = 2$ region and are not considered further. The EPR properties of the compounds studied are summarized in Table I.

Five of the complexes ($[MoCl_6]^{3-}$, $[MoCl_5(H_2O)]^{2-}$, $Mo(acac)_3$, $Mo(8\text{-}O\text{-}quin)_3$, and $Mo[S_2P(OEt)_2]_3$) display similar very broad, axial or slightly rhombic spectra centered at $g =$ 4 and 2 (e.g., Figure 1). These signals are highly temperature dependent, disappearing above 30 K, and are not saturated at relatively high microwave power (3 mW). The similarity of the spectra of the three tris-chelate complexes to those of $[MoCl_6]^{3-}$, known to be octahedral in the solid state,[18] and $[MoCl_5(H_2O)]^{2-}$ indicates that the spectra are due to monomeric Mo(III) in an approximately octahedral environment. Similar signals have been reported previously for $Mo(acac)_3$. Further, although the tris(diethyldithiophosphate) complex of Mo(III) has apparently not been reported previously, the analogous difluorodithiophosphate complex is known to be monomeric, presumably octahedral.[19] This type of spectrum is typical of the $\pm^1/_2$ Kramers' doublet of an $S = {}^3/_2$ system subjected to a relatively large zero-field splitting and an axial

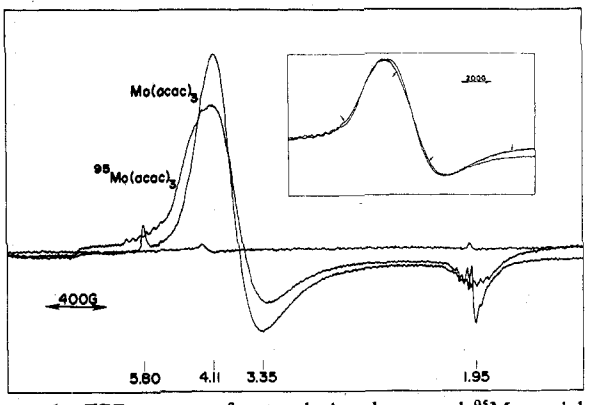

Figure 1. EPR spectra of natural abundance and ^{95}Mo-enriched $Mo(acac)_3$, compared to a base line obtained with the cavity under the same conditions. Inset: Comparison of spectrum estimated by assuming $A_\perp(^{95}Mo) = 60$ G and ^{95}Mo-enriched spectrum in $g_\perp$ region. Arrows indicate this estimated spectrum. Conditions of EPR spectroscopy: microwave frequency, 9.2 kHz; microwave power, 3 mW; modulation amplitude, 10 G; magnetic field sweep rate, 1000 G min^{-1}; time constant, 0.3 s; sample temperature, 13 K; instrument gain, 1250. In the inset, the amplitude and microwave power were adjusted to match the simulation and the $^{95}Mo(acac)_3$ spectrum as closely as possible.

or rhombic ligand field.[9,20] For such a system with axial symmetry, values of $g_\perp = 4$ and $g_\parallel = 2$ are predicted; small rhombic distortions will split the $g = 4$ line in an approximately symmetrical fashion. The observation of this type of signal for the $[MoCl_6]^{3-}$ ion indicates either that the symmetry is degraded from cubic in solution or that even in 12 N HCl hydrolysis to $[MoCl_5(H_2O)]^{2-}$ is rapid. Experiments to date have not resolved whether the disappearance of these signals at higher temperatures is due to broadening caused by very fast spin–lattice relaxation or to thermal population of an excited state with no detectable EPR signal, if the zero-field splitting is comparable to kT.

$Mo(acac)_3$ in an $Al(acac)_3$ matrix has been studied previously by Jarrett[8a] and Schoffman.[8b] The former reported an axial spectrum ($g_\perp = 3.94$ and $g_\parallel = 1.94$), while the latter obtained a rhombic spectrum with g values of 4.3, 3.5, and 1.9. These compare favorably with the present work (spectral features at $g = 4.11$, 3.35, and 1.95; $4.11 > g_x$, $3.35 < g_y$, $1.95 \sim g_z$), considering the width of the signals and the difference in samples (crystals vs. dilute glasses). In order to assure ourselves that the observed line width ($\sim$250 G at $g = 4.11$) was not due to magnetic interactions caused by aggregation during freezing, we ran parallel experiments in which the $Mo(acac)_3$ (final concentration $\leq$1 mM) was diluted with 0.5 M $Al(acac)_3$. Although no reduction in the line width was observed, the spectra with ^{95}Mo were also obtained in the presence of 0.5 M $Al(acac)_3$.

A feature at $g = 5.80$ is present in all preparations (Figure 1); its splitting by ^{95}Mo (see below) shows that it also originates from a molybdenum-containing species. The most reasonable assignment is to the g_z component of the $\pm^3/_2$ Kramers' doublet of the $S = {}^3/_2$ spin system of $Mo(acac)_3$. This is supported by its position (the expected g value[20] is $\sim 3g_\parallel$ or 5.85 in this case) and by the temperature dependence of the two signals. As the temperature is decreased from $\sim$13 to 4 K under nonsaturating conditions, the intensity of the $g =$ 5.80 line increases while that of the broad $g = 4$ and 2 signal decreases. This is consistent with a negative value of the zero-field splitting. Recent low-temperature magnetic susceptibility data[21] on $Mo(acac)_3$ could be fit with $D = +7.0$

(16) Preliminary experiments comparing the reaction of $(NH_4)_3[MoCl_6]$ and $(NH_4)_2[MoCl_5(H_2O)]$ with aqueous acetylacetone indicated that the hexachloro complex gave significantly better yields of $Mo(acac)_3$, as shown previously (ref 15); consequently, it was used throughout these experiments. Double integration of the EPR spectrum showed that yields of $Mo(acac)_3$ were consistently $\sim$50%.
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or -6.3 cm^{-1}. Our results clearly establish that the latter is correct.

That neither Jarrett or Schoffman were able to observe the hyperfine interaction due to natural abundance isotopes with $I = {}^5/_2$ (15.7% ^{95}Mo, 9.5% ^{97}Mo) is thus not surprising, since the A (^{95}Mo) observed in Mo(V) compounds is typically 70 G ($\sim$8 mK) at most. In order to ascertain whether Mo(III) complexes show comparable hyperfine, we prepared Mo(acac)$_3$ enriched in ^{95}Mo (97%). Figure 1 compares the EPR spectra of Mo(acac)$_3$ containing natural abundance and enriched ^{95}Mo. It is immediately obvious that there is a significant broadening of both components of the spectrum due to the $\pm{}^1/_2$ Kramers' doublet (centered at $g = 3.68$ and 1.95), as well as a splitting of the feature at $g = 5.80$, upon incorporation of ^{95}Mo. A crude simulation, obtained by recording the $g_\perp$ portion of the natural abundance spectrum six times at positions corresponding to an assumed hyperfine of 60 G and summing on a minicomputer, is compared to the $g = 4$ region of the natural abundance spectrum in the inset of Figure 1. In view of the natural line width, the approximations made in this approach (purely axial symmetry, coincident **g** and **A** tensors), and the neglect of the contribution of the naturally occurring (15.7%) ^{95}Mo to the observed line width, the fit is extremely good, indicating a value of $A_\perp(^{95}\text{Mo}) = 60 \pm 5$ G (10 ± 1 mK) for the $\pm{}^1/_2$ Kramers' doublet. The presence of residual amounts of Mo(V) impurities in the $g = 2$ region made a similar procedure impossible, although there is clearly some broadening of the $g_\parallel$ resonance as well. The value of A_z for the $\pm{}^3/_2$ Kramers' doublet, determined directly from the spectrum, is 45 G (12.2 ± 0.5 mK). Simultaneous direct observation of hyperfine coupling constants for pairs of related Kramers' doublets appears to be relatively rare in the literature. Similar broadening was observed when ^{95}Mo was incorporated into Mo(8-O-quin)$_3$ and Mo[S$_2$P(OEt)$_2$]$_3$, but due to the quality of the spectra[22a] and the lack of a suitable isostructural diamagnetic diluent,[22b] no attempts at spectral approximation were made.

Although the diethyldithiocarbamate ligand might be expected to give a complex analogous to those obtained with the ligands discussed above, no evidence for an $S = {}^3/_2$ species was observed in the low-temperature EPR spectrum. Instead, a mixture of two complexes, whose relative concentrations varied from preparation to preparation, was observed near $g = 2$; the total yield as determined by double integration never exceeded 20%, based on Mo. Due to different saturation characteristics, the spectra could be partially resolved by varying the microwave power. The observed average g values of 1.989 (axial low-power signal) and 1.98 (broad high-power signal) are very close to those reported by other workers, and variously assigned to a dimeric Mo(III) species,[5] [Mo(dtc)$_3$]$_2$, or to a monomeric, eight-coordinate Mo(V) species,[23] Mo(dtc)$_4^+$. Similarly, 2-aminothiophenol does not give an EPR spectrum attributable to a monomeric tris complex of Mo(III); only an apparently isotropic signal at $g \sim 2.00$ is observed. This is similar to the results reported recently for the Mo(NHC$_6$H$_4$S)$_3^-$ complex[24] and suggests that the Mo(NH$_2$C$_6$H$_4$S)$_3^0$ complex, if produced initially, may be oxidized by trace amounts of disulfide in the ligand.

Reaction of 8-mercaptoquinoline with (NH$_4$)$_3$[MoCl$_6$] gives a yellowish brown toluene solution, together with a brown solid which remains at the interface of the two layers. This agrees with the findings of Lindoy et al.,[25] who reported the formation of a brown polymer in refluxing ethanol. Examination of the supernatant by EPR spectroscopy revealed the presence of a paramagnetic species (Figure 2), which by double integration accounted for only 2–4% of the total Mo. The observed rhombic spectrum ($g = 2.29$, 2.15, 1.97; $g_{av} = 2.14$) is not characteristic of the Mo(III) species described above and lies far outside the range observed for Mo(V) complexes.[26] Substitution of ^{95}Mo gave no splitting or detectable broadening of the spectrum (Figure 2), even though the lines are relatively narrow ($\sim$45 G). This suggests that the observed spectrum may not be due to a molybdenum species at all but instead to an organic free radical. Indeed, highly anisotropic signals with $g_{av} = 2.08$–2.09 have been observed in crystals of cysteine hydrochloride irradiated at low temperature.[27] The stability of this species in contact with aqueous media at room temperature, the anomalously high microwave power required to saturate the signal (>1 mW at 13 K), and the fact that no such signals have been observed in previous work on Mo(V) complexes of 8-mercaptoquinoline[28] all suggest that the observed signal may be due to a radical stabilized by a diamagnetic molybdenum complex. An alternative interpretation is that the signal originates from a mono- or polynuclear Mo complex with one unpaired electron. The former would require a low-spin Mo(III) complex, of which there is apparently one well-established case,[29] while the latter would require a polynuclear mixed valence complex, with intramolecular antiferromagnetic coupling of the spins of the Mo atoms to yield an $S = {}^1/_2$ ground state. The absence of a detectable hyperfine interaction with ^{95}Mo indicates that the unpaired electron would have to reside in orbitals with essentially no s character and hence no appreciable electron density at the Mo nucleus. This is not unprecedented in transition-metal chemistry. For example, Co^{2+} (d^7) normally shows a relatively large hyperfine coupling to the ^{57}Co nucleus. When Co^{2+} is doped into tet-

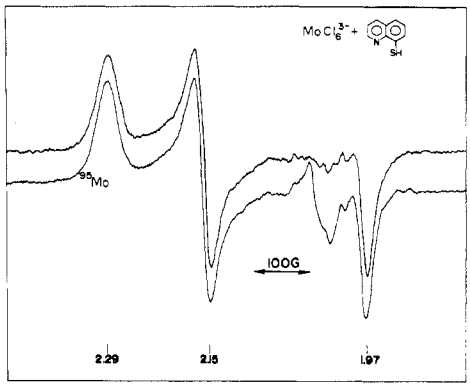

Figure 2. EPR spectra of the toluene supernatant from the reaction of 8-mercaptoquinoline with (NH$_4$)$_3$MoCl$_6$ and (NH$_4$)$_3{}^{95}$MoCl$_6$ as described in the text. Conditions of EPR spectroscopy were as in Figure 1 except for the following: microwave power, 100 μW; magnetic field sweep rate, 250 G min^{-1}; time constant, 1.0 s; instrument gain, 5000 (^{95}Mo), 6300 (natural abundance Mo).

(22) (a) The Mo(8-O-quin)$_3$ complex was formed in only 5–10% yield; (b) the dithiophosphate complex, although formed in $\sim$90% yield by double integration, appeared to aggregate partially even during rapid freezing and gave somewhat irreproducible spectral line widths.
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rahedral sites in materials such as ZnS, the observed hyperfine interaction is reduced by 2 orders of magnitude from the normal value.[30] At the moment, we have no means of distinguishing between these alternatives.

Conclusions

At temperatures below 30 K, monomeric Mo(III) complexes based on an octahedral geometry exhibit broad axial or rhombic EPR signals, centered at $g = 4$ and 2. Even with the large line widths, substitution of ^{95}Mo results in significant broadening of the signal with $A_\perp(^{95}\text{Mo})$ on the order of 60 G for $Mo(acac)_3$. This suggests that in enzymes such as nitrogenase[6] and nitrate reductase,[2b,7] which display similar signals but with even narrower lines (due to different relaxation properties of the chromophore), substitution of ^{95}Mo should result in significant broadening or splitting of the signal, if it is indeed due to Mo(III). The failure to observe this effect in the ^{95}Mo-substituted Mo–Fe protein of nitrogenase[2b,9] is therefore further evidence that the characteristic EPR signal is *not* due to a simple Mo(III) site. Assignment of narrow signals at $g \sim 2$, observable at >77 K, to Mo(III) in enzymes containing only isolated molybdenum sites is questionable. Similar signals reported by others[5] for Mo(III) complexes are almost certainly due to polynuclear mixed-valence complexes or monomeric Mo(V) impurities.

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Registry No. $Mo(acac)_3$, 14284-90-3; $Mo[S_2P(OEt)_2]_3$, 72967-95-4; $MoCl_6^-$, 15203-34-6; $MoCl_5(H_2O)^{2-}$, 73199-11-8; $Mo(8\text{-O-quin})_3$, 26191-06-0; $Mo(Et_2dtc)_3$, 15740-71-3; $Mo(o\text{-}H_2NC_6H_4S)_3$, 73199-10-7; $Mo(8\text{-S-quin})_3$, 73210-22-7; $^{95}Mo(acac)_3$, 73199-09-4; $^{95}Mo(8\text{-S-quin})_3$, 73210-21-6; $(NH_4)_3MoCl_6$, 18747-24-5; $(NH_4)_3{}^{95}MoCl_6$, 73199-08-3.

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Polarized Electronic Absorption Spectra of (Ethylenediamine)dichloropalladium(II)

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Optical absorption spectra of single crystals of $Pd(en)Cl_2$ are reported for temperatures of 300 and 5 K from 18 000 to 34 000 cm^{-1}. Spectra were recorded for linearly polarized light with the electric vector parallel to the molecular twofold symmetry axis (*b*) and parallel to the stacking of the nearly planar molecules (*c*). In contrast to the corresponding platinum compound, $Pt(en)Cl_2$, the spectra of the $Pd(en)Cl_2$ showed no intensity enhancement whatsoever in the stacking direction of the molecules. Also, there was no evidence in the palladium compound for the intermolecular electron-transfer transitions to ionic states that were observed for the platinum compound. The $Pd(en)Cl_2$ crystal spectra in the measured region were comprised primarily of ligand field bands. Shifts of d–d transition energies from the resolved bands in aqueous solution were determined to be similar to the shifts observed for $PtCl_4^{2-}$ in Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$.

Introduction

Both $Pt(en)Cl_2$ and $Pd(en)Cl_2$ crystallize with the nearly planar molecules stacked face to face.[1] Earlier, polarized crystal spectra were reported for $Pt(en)Cl_2$.[2] It was shown that an intense, electric dipole allowed transition in $Pt(en)Cl_2$, polarized normal to the molecular plane, had been shifted from 49 000 cm^{-1} where it appears in the solution spectrum to 37 500 cm^{-1} by crystal perturbations. As a consequence, those dipole-forbidden d–d transitions that were polarized in the stacking direction of the molecules were strongly enhanced in intensity. Such behavior is similar to that observed for Magnus' green salt (MGS), $[Pt(NH_3)_4][PtCl_4]$.[3-5] In addition, the $Pt(en)Cl_2$ crystal spectra possessed two bands which were attributed to intermolecular electron-transfer transitions with ionic exciton excited states. The palladium complex has the $4d^8$ electronic configuration which is comparable to the $5d^8$ of the platinum compound, and the present work provides a quantitative comparison between the spectra of the two compounds.

Experimental Section

$Pd(en)Cl_2$ was prepared by the method of Watt and Carter.[6] Single crystals, prepared by the slow evaporation of aqueous solutions, generally had the form of needles or long, flat platelets. One of the platelets was mounted on a four-circle X-ray diffractometer. A sufficient number of reflections were observed so crystallographic axes could be identified and refined by standard programs. The indicated crystallographic axes and angles were $a = 12.407$ Å, $b = 8.118$ Å, $c = 6.739$ Å, $\alpha = 89.97°$, $\beta = 89.78°$, and $\gamma = 90.00°$. These values were in very satisfactory agreement with the structure reported by Iball et al., viz., orthorhombic $C222_1$, with $a = 8.116$ Å, $b = 12.416$ Å, and $c = 6.736$ Å. Note that we have interchanged the *a* and *b* axes, which have equivalent symmetry, from the convention of Iball et al. in order to retain the convention which was utilized in our earlier spectral study of $Pt(en)Cl_2$. The large faces of the platelets were identified by the diffractometer as (100) with the long dimension or the needle axis being along the *c* axis. For this face the electric vectors for the two transmitted waves are aligned along the *c* axis and along the *b* axis, respectively. Examination of the crystals between crossed polarizers with a quartz wedge indicated that the index of refraction for the *c*-polarized wave (n_c) was less than n_b. The index n_c was found by the Becke line method with a set of index of refraction standard

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