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Crystal Structure and Properties of [Pt(NH$_3$)$_4$Cl](HSO$_4$)$_2$, a Tetraammine Analogue of Wolfram's Red Salt

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Crystals of [Pt(NH$_3$)$_4$Cl](HSO$_4$)$_2$ were obtained by the oxidation by hydrogen peroxide of tetraammineplatinum(II) dichloride in 50% H$_2$SO$_4$. The structure was determined by X-ray crystallography: a = 5.466 (3) Å, b = 10.280 (3) Å, c = 10.633 (3) Å, β = 93.16 (3)°, V = 596.57 Å^3, space group $P2_1/c$, Z = 2, ρ_{calcd} = 2.74 g/cm^3. Refinement on 636 reflections with $F^2 > 3.0\sigma(F^2)$ yielded final discrepancy indices of R_F = 0.034 and R_w = 0.044. The structure and properties are typical for such one-dimensional systems. The crystals are highly dichroic and display an absorption at 19 500 cm^{-1} that is polarized parallel to the stacking direction. The bisulfate anions are hydrogen bonded to each other to form dimers. There is also extensive hydrogen bonding between the amine hydrogens and bisulfate oxygens, which stabilizes the crystal structure.

Introduction

One-dimensional solids have been the subject of intense investigation recently.[1] Crystals of mixed-oxidation-state platinum complexes in which the average oxidation state of the platinum is +3 are some of the oldest examples of such solids. These crystals are composed of chains of alternating platinum(II) and platinum(IV) complexes which are connected through a halogen. These crystals are also examples of mixed-oxidation-state compounds because in the ground state the charges are localized. Examples of such compounds are readily synthesized from neutral complexes and results in compounds with an empirical formula [PtA$_2$X$_3$], where A represents an amine or other neutral ligand and X a halogen.[2] Similar cationic and anionic species [PtA$_3$X$_2$]$^+$ and [PtAX$_4$]$^-$ can also be prepared.[3,4] In addition, analogous compounds consisting of chains of Pd(II)–Pt(IV) and Pd(II)–Pd(IV) complexes have been prepared.[5] The crystals of all of these materials have certain common properties: a metallic luster, remarkable dichroism, and weak, semiconducting conductivity[6] typical of one-dimensional compounds.

Surprisingly, cationic compounds with a new 2+ charge are also known to crystallize in one-dimensional chains under the right circumstances. The oldest known example is the compound [Pt(NH$_2$(C$_2$H$_5$))$_4$Cl]Cl$_2$, which was first prepared by Wolfram in 1900 by the partial oxidation of a solution of [Pt(NH$_2$(C$_2$H$_4$))$_4$]Cl$_2$.[7] This compound is known as Wolfram's Red Salt. By careful cocrystallization of the platinum(II) and platinum(IV) tetrakis(ethylamines), both this compound and the corresponding bromide were later prepared by Reihlen.[8] The bromide compound is dark green. Reihlen reported that the synthesis of these "Pt(III)" species was possible only when ethylamine was the ligand. Other tetraaminoplatinates failed to cocrystallize. Only two exceptions to this finding have been reported: [Pt(NH$_2$(C$_3$H$_7$))$_4$Cl]Cl$_2$[9] and [Pt(en)$_2$Cl](ClO$_4$)$_2$.[10]

In this paper we report the preparation, crystal structure, and spectral properties for the tetraammine analogue of

Wolfram's Red Salt, [Pt(NH$_3$)$_4$Cl](HSO$_4$)$_2$. The structure and properties of this compound provide insights into the nature of the bonding in the chains and suggest why this particular compound has proven so difficult to prepare.

Experimental Section

Preparation of [Pt(NH$_3$)$_4$Cl](HSO$_4$)$_2$. The complex [Pt(NH$_3$)$_4$]Cl$_2$ was prepared by literature methods. About 20 mg of [Pt(NH$_3$)$_4$]Cl$_2$ was placed in a test tube to which 10 mL of 50% H$_2$SO$_4$ was added. No attempt was made to dissolve the platinum complex. To this 1–2 drops of 30% H$_2$O$_2$ was added. After several days, an orange powder had formed on top of the undissolved starting material. After 6–8 weeks, long, acicular crystals of [Pt(NH$_3$)$_4$Cl](HSO$_4$)$_2$ had grown. The crystals are orange–pink and are very dichroic. The appear dark orange when the plane of polarization of the light is parallel to the needle axis and are nearly colorless when it is perpendicular. The crystals were filtered off and washed with ethanol. The compound is soluble in water and results in colorless solutions.

Structure Determination and Solution. While moderately sized crystals were synthesized, rotation photographs about the needle axis indicated that all were twinned. Finally a fine needle 0.05 × 0.07 × 0.41 mm was chosen that proved to be single. The crystal was mounted on a glass fiber with epoxy resin. The needle direction was nearly parallel to the fiber. The crystal was indexed, and data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator and a fine-focus molybdenum X-ray tube. The takeoff angle was 4.2°. The centered settings of 25 reflections with 12° < 2θ < 35° were used to determine the cell constants a = 5.466 (3) Å, b = 10.280 (3) Å, c = 10.633 (3) Å, β = 93.16 (3)°, V = 596.57 Å,^{3} ρ_{calcd} = 2.74 g/cm^3, and Z = 2. The systematic absences 0k0, k = 2n + 1, and h0l, l = 2n + 1, uniquely identified the monoclinic space group as $P2_1/c$. Two octants ($h,-k,l$ and $h,-k,-l$) were collected at 22 °C with use of the θ–2θ scan technique to a maximum value of 2θ of 45°. The vertical aperture was 4.0 mm, and the horizontal aperture was determined by (1.50 + 1.00 tan θ) mm. The scan width was calcualted from (0.60 + 0.35 tan θ)°. The final scan speed was required to reproduce an intensity 50 times greater than $\sigma(I)$ or to scan the peak in no more than 60 s. Of the 830 unique reflections collected only the 636 reflections with $F^2 > 3.0\sigma(F^2)$ were used during refinement. The value of the p factor used to calculate $\sigma(F^2)$ was 0.02.[11] Three standard reflections were monitored after every hour of beam exposure during data collection and displayed no systematic variation in intensity.

Because the linear absorption coefficient was 129.5 cm^{-1}, some type of absorption correction was necessary. Since the crystal was very small and the faces could not be accurately determined, an empirical absorption correction was attempted. However, problems arose with this method. Sets of ψ scans performed for reflections with χ > 75° displayed a regular variation in absorption. However reflections with χ < 60° had very sharp spikes in the scan. These corresponded to ψ settings where ω was very different from θ and brought the needle more lengthwise into the beam. These spikes were a function of ω.

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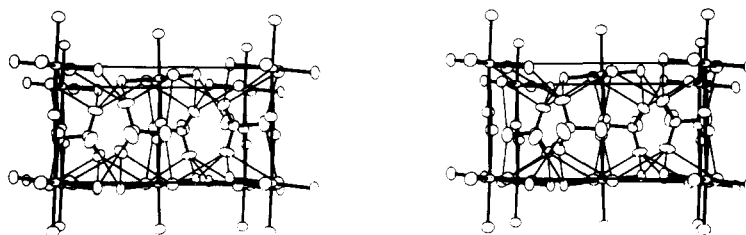
Figure 1. ORTEP stereoview of the unit cell of $[Pt(NH_3)_4Cl](HSO_4)_2$. The stacking axis is the a axis and the horizontal axis is b. The thin lines represent N–H$\cdots$O hydrogen bonds.

Table I. Positional Parameters for the Atoms of $[Pt(NH_3)_4Cl](HSO_4)_2$

atom	x^a	y	z
Pt	0	0	0
Cl	0.423 (1)	0.0084 (7)	0.0027 (7)
S	0.5346 (5)	−0.1385 (3)	0.3561 (3)
O1	0.720 (1)	−0.1986 (8)	0.2849 (8)
O2	0.556 (2)	0.0098 (7)	0.330 (1)
O3	0.289 (1)	−0.1773 (8)	0.3214 (8)
O4	0.589 (2)	−0.1570 (9)	0.4925 (7)
N1	0.008 (2)	0.057 (1)	0.1854 (8)
N2	0.043 (2)	−0.1917 (8)	0.0540 (9)

^{a} Estimated standard deviations in the last figures are given in parentheses in this and all subsequent tables.

Table II. Intramolecular Distances (Å) and Angles (Deg) for $[Pt(NH_3)_4Cl](HSO_4)_2$

Pt–N1	2.056 (9)	S–O1	1.439 (8)
–N2	2.062 (8)	–O2	1.555 (7)
Pt(IV)–Cl^a	2.310 (7)	–O3	1.431 (8)
Pt(II)–Cl	3.151 (8)	–O4	1.477 (8)
Cl–Cl′ ^{b}	0.86 (1)		
N1–Pt–N2	90.6 (4)	O1–S–O2	105.3 (6)
–Cl	90.5 (3)	–O3	115.1 (6)
N2–Pt–Cl	86.2 (3)	–O4	110.6 (5)
Cl′–Cl–Pt	166 (1)	O2–S–O3	107.9 (6)
Pt–Cl–Pt	176.2 (5)	–O4	106.6 (6)
		O3–S–O4	110.7 (6)

^{a} The numbers in parentheses refer to the oxidation state.
^{b} The prime sign refers to an atom related by the inversion center.

The empirical correction program CAMEL JOCKEY WITH THREE HUMPS[12] did an excellent job in correcting for the absorption with changing ϕ but could not smooth the ω spikes. As all data collection was done in the bisecting position ($\omega = 0$), the importance of the ω functions was problematical. Nevertheless, an analytical correction with use of the program AGNOST was performed. The crystal was approximated by a rectangular box bounded by the faces perpendicular to a, b, and c; the a axis being the determined needle axis. The similarity of the widths (0.05 and 0.07 mm) and the fact that they are quite small makes such an approximation valid.

All calculations were performed on the IBM 370/165 computer at the University of Kentucky Computing Center. The programs used included Ibers' NUCLS least-squares program (based on the Busing–Levy ORFLS program) Zalkins' FORDAP Fourier program, the Busing–Levy ORFFE error function program and Johnson's ORTEP thermal ellipsoid plotting program. Corrections for anomalous dispersion were included in the scattering factor tables for platinum, chlorine and sulfur. The least-squares program minimized the function $w(|F_o| - |F_c|)$,^{2} where the weighting factor $w = 1/\sigma(F_o)^2$.

From the volume of the cell it was determined that $Z = 2$. Since the space group $P2_1/c$ has four general positions, the platinum was required to be situated at a special position with symmetry $\bar{1}$. From the Patterson map the position (0, 0, 0) was chosen. All the other atoms were located in a difference Fourier map after refinement of the scale factor and platinum isotropic temperature factor. Further refinements of atomic positions and anisotropic thermal parameters resulted in final residuals of $R_F = 0.034$ and $R_w = 0.044$. The final difference Fourier map displayed no peaks of chemical significance. The hydrogen atoms bonded to the nitrogens or the bisulfate oxygen were not observed in the maps and were not refined. Table I lists the atomic positions and their errors. Table II lists the intramolecular bond distances and angles.

Spectra. UV–visible spectra were recorded on a Cary 14 spectrophotometer equipped with a Hamamatsu R-928 photomultiplier tube and a DXN high-intensity light source. For crystal spectroscopy two Glan-Thompson polarizers were used: one in the reference beam and one placed behind the sample. The infrared spectrum was recorded on a Perkin-Elmer 621 spectrophotometer. The sample was in the form of a KBr pellet.

Results

As mentioned in the Introduction, it has proved nearly impossible to synthesize mixed-oxidation-state platinum compounds analogous to Wolfram's Red Salt with amines other than ethylamine. The major differences in the synthesis reported here is the use of 50% H_2SO_4 as the solvent, which results in bisulfate as the anion. Even in the presence of excess chloride ion, bisulfate is the anion in the crystal. The synthesis is straightforward. Oxidation by H_2O_2 was the method originally used in the synthesis of Wolfram's Red Salt.[7]

The structure of the cationic platinum complex chain [Pt(NH₃)₄Cl] is very similar to those reported for other compounds of this type.[13–15] The ORTEP drawing for the unit cell is given in Figure 1. The crystal is composed of infinite chains of stacked platinum complexes. These chains are interconnected by hydrogen bonding between the amine hydrogens and the oxygens of the bisulfate anions. The chains are composed of alternating levels of *trans*-dichlorotetraammineplatinum(IV) and tetraammineplatinum(II). The chlorine atoms serve as a bridge between the two cationic complexes. The amine ligands are in an eclipsed configuration as viewed down the stacking axis. The bridging chlorine atom is not equidistant between the Pt(II) and Pt(IV). The Pt(IV)–Cl distance is 2.310 Å while the Pt(II)–Cl distance is a longer 3.158 Å, suggesting the platinums are in the two different oxidation states in the crystal. Similarly, it was shown that isotopic exchange of platinum between the complexes in the different oxidation states in [Pt(en)Br₂][Pt(en)Br₄] did not occur.[16] All these data suggest that the charge is localized.

As has been observed previously for all other "Pt(III)" solids, there is crystallographic disorder in $[Pt(NH_3)_4Cl](HSO_4)_2$. The unit cell reported consists of only a single Pt–Pt repeat distance along the a axis. The alternating chain structure would require a Pt(IV)–Pt(II)–Pt(IV) distance as the unit cell. Rotation photographs about the a axis (the stacking direction) showed diffuse streaking, which suggests doubling of this axis. However, these data were not observed on the diffractometer. Ryan and Rundle[14] explained this disorder by suggesting that the individual chains are ordered but the arrangement of chains

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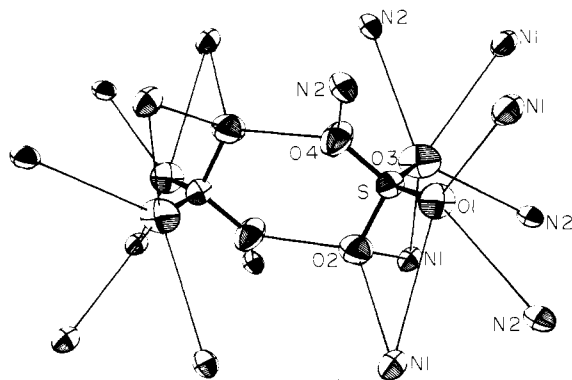
Figure 2. Arrangement of the bisulfate anions in [Pt(NH₃)₄Cl](H-SO₄)₂ illustrating hydrogen bonds to coordinated ammonias. The unlabeled atoms are related to those that are labeled by an inversion center. The atoms are represented by their thermal ellipsoids of 50% probability.

in the crystal is disordered. The result of this disorder is that the bridging chlorine atom is disordered about the Pt–Pt midpoint and must be refined with an occupancy of 50%. In [Pt(NH₃)₄Cl](HSO₄)₂ the two half-chlorine sites are only 0.86 (1) Å apart. This is too short a distance to allow for both sites to be occupied simultaneously. As an additional consequence of this disorder, each platinum in the structure is actually a composite, being 50% Pt(II) and 50% Pt(IV). There is no indication in any of the nitrogen thermal parameters to suggest that there is any significant difference in the Pt–N bond lengths in the complexes of different oxidation states.

The platinum(IV)–chlorine and two platinum–nitrogen bond lengths are all typical, being 2.310 (7), 2.056 (9), and 2.062 (8) Å, respectively. The two independent Pt–N distances are identical within experimental error. These distances can be compared to those reported in *trans*-[Pt(NH₃)₄Cl₂]Cl₂, where Pt–Cl was 2.25 Å and Pt–N was 2.03 Å.[17] Typical distances for Pt(II) are Pt–Cl = 2.34 Å and Pt–N = 2.06 Å.[18] It is interesting that all the distances reported here are significantly longer than those previously determined for Wolfram's Red Salt where the corresponding Pt–Cl bond length was 2.26 Å and the Pt–N distance was 1.97 Å.[15]

The symmetry of the unit cell for [Pt(NH₃)₄Cl](HSO₄)₂ is the lowest observed for a "Pt(III)" crystal. While $P2_1/c$ is quite common, most of the previously reported structures of similar compounds crystallized in either a tetragonal cell or a C-centered orthorhombic cell. The reduction of symmetry to $P2_1/c$ has several consequences. First, the plane consisting of the four nitrogens and the platinum is not defined by a crystallographic mirror plane. However, the [Pt(NH₃)₄] moiety is rigorously planar. Second, the chlorine atom is not required to be perpendicular to this plane. The chlorine sites lie off the a axis, and the Pt–Cl–Pt bond angle is 176.2 (5)°.

The arrangement of the bisulfate ions within the unit cell is shown in Figure 2. In previously reported structures for the alkali metal bisulfates[19-20] and ammonium bisulfate[21] the anion has always been found hydrogen bonded to itself to form one of two arrangements, either a linear polymer or a dimer. The bisulfates in [Pt(NH₃)₄Cl](HSO₄)₂ form dimers. The two halves are related by a crystallographic inversion center. The bisulfates are joined through a relatively short bond of 2.58 (1) Å (oxygen to oxygen). Again, this is similar to the distances of 2.68 and 2.62 (3) Å reported for bisulfate dimers

Table III. Hydrogen-Bonding Distances (Å)

O1–N1	2.92 (1)	O3–N2	3.08 (1)
–N2	3.10 (1)	–N1	3.17 (1)
–N1	3.27 (1)	–N1	3.17 (1)
–N2	3.47 (1)	–N2	3.18 (1)
O2–O4′	2.58 (1)	O4–N2	2.97 (1)
–N1	3.02 (2)	–N2	3.46 (1)
–N1	3.33 (2)		

in KHSO₄ and the mixed salt Rb₀.₄₅K₀.₅₅HSO₄, respectively. While the hydrogen of the bisulfate was not observed during refinement, its presence is clearly indicated by the variation in sulfur–oxygen bond lengths. The hydrogen is strongly bound to O2 as the S–O2 bond is significantly longer than any other sulfur–oxygen bond. The effect of the interionic hydrogen bond also lengthens the S–O4 bond and results in it being about 0.04 Å longer than those on the outside of the dimer. All of these bond distances are quite comparable to those in the simple salts. In addition, as is indicated by the two ORTEP drawings, the hydrogen bonding between the anions and the ammine ligands is extensive. These hydrogen bonds are within the average length of 2.8–3.4 Å for O–N hydrogen bonds reported in ref 22. Each ammine ligand is bound to at least three different bisulfate oxygens, and the two nonbridging oxygens are bound to at least three nitrogens. A listing of hydrogen-bond lengths is provided in Table III.

The dimerized bisulfate anions can be treated like an a H₂S₂O₈²⁻ entity. This group has C_{2v} symmetry. The sulfur–oxygen stretching modes observed in the infrared spectrum should therefore appear similar to those for a bridging SO₄²⁻ ligand. Indeed, ν_3 modes are observed at 1187, 1140, 1100, and 1050 cm⁻¹ and ν_4 modes at 613 and 595 cm⁻¹, which are comparable to those of bridging sulfates.[23] The only other strong bands in the IR spectrum are the O–H and N–H stretches observed at about 3200 cm⁻¹.

The electronic spectrum of [Pt(NH₃)₄Cl](HSO₄)₂ was recorded for the solid in KBr and for a crystal. As the crystals grew as very elongated needles, it proved difficult to find one suitable for spectroscopy. Only one was obtained that was wide enough to cover the slit cut in the brass mounting plate. This crystal was too thick (~0.1 mm) to allow the absorptions to be fully recorded. Also, because the faces were very small, it proved impossible to ascertain exactly which face was being observed. However, this point is moot since the extinctions are exactly parallel and perpendicular to the a axis, which represents the stacking direction. The spectrum for light polarized along the stacking direction displayed no absorption below 17 000 cm⁻¹. At this point the absorption increased sharply and quickly became too great to measure. This absorption gives rise to the orange color observed for these crystals. When the light was polarized perpendicular to the needle, no absorptions were observed below 20 000 cm⁻¹. In fact, the only band observed was a shoulder at about 23 260 cm⁻¹. This band can be assigned to a d → d band located on the Pt(IV) complex which has been observed at a similar energy in other Pt(IV) complexes. For example, Yamada and Tsuchida reported that the solution spectrum of [Pt(NH₂-(C₂H₅))₄Cl₂]Cl₂ displayed weak absorptions at 20 800 and 25 600 cm⁻¹.[24] Similar bands have been reported at 21 600 and 29 100 cm⁻¹ in [Pt(NH₃)Cl₅]⁴⁻ and 22 100 and 28 000 cm⁻¹ in [PtCl₆]²⁻.[25] On the other hand, the platinum(II) tetraammine does not display any absorbances below 34 800 cm⁻¹.[26]

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The bands observed for light polarized along the a axis must be due to some form of inter-platinum transition resulting from the solid-state structure. When $[Pt(NH_3)_4Cl](HSO_4)_2$ was ground with potassium halides, it was quite obvious that the color changed from orange to yellow. This change can be attributed to the presence of a transition at $15\,400$ cm^{-1}, which was clearly not present in the crystal. The spectrum of the pellet also displayed a band centered at about $19\,500$ cm^{-1}, which is presumed to be the maximum for the a-polarized transition.

Discussion

The electron structure of the crystal can be qualitatively formulated from band theory. Since there is no great difference between the xy planes for the platinum(II) and platinum(IV) constituent complexes, the $d_{x^2-y^2}$ and d_{xy} orbitals for each form a single narrow band. Similarly, the d_{xz} and d_{yz} orbitals are quite similar in the chain and should form a somewhat broader band. The important band is the one formed from the platinum d_{z^2} orbitals. In the isolated *trans*-dichlorotetraammineplatinum this orbital forms an a_{1g} representation in D_{4h} symmetry. It is derived from the e_g antibonding pair of an octahedral complex. As such it has a fairly high energy. On the other hand, the d_{z^2} orbital for the platinum(II) complex is essentially nonbonding with respect to the ligands. Therefore, it is of relatively low energy. The d_{z^2} band gap that would result from a crystal composed of isolated Pt(II) and Pt(IV) complexes would then represent the difference in energy between the d_{z^2} orbitals in these complexes of different geometry. As the chain is formed, the energy of this band gap will depend on the Pt–Pt distance and on the difference between the bridging Pt(II)–Cl distance and the Pt(IV)–Cl distance (called d). As the two platinums approach each other the Pt(II) d_{z^2} orbital will increase in energy because of the approach of the bridging halogen. As this happens the energy difference between d_{z^2} (IV) and d_{z^2} (II) will decrease. Similarly, as the Pt(IV)–Cl and Pt(II)–Cl distances becomes more equal, the platinums become more Pt(III)-like. Indeed, if $d = 0$, the platinums are both equivalent and the d_{z^2} band gap goes to zero.

The electronic band structure for a chain of the formula $[Pt(NH_3)_4Cl]^{2+}$ has recently been calculated by Whangbo and Foshee using the extended Hückel method.[27] Their results confirmed the simple qualitative picture. In the case where $d = 0$, the two platinums were formally d^7 Pt(III) atoms and there was only one d_{z^2} band. This resulted in a minimum stabilization energy for the solid. The maximum stabilization of ~ 40 kcal/mol was calculated to occur at $d = 0.48$ Å. The observed d in Wolfram's Red Salt was 0.435 Å. However, it is harder to relate this calculation to the structure of $[Pt(NH_3)_4Cl](HSO_4)$ because in this case the Pt–Cl–Pt chain is not linear. The difference in the platinum–chlorine distances gives a value of 0.43 Å, which is nearly identical with that in the linear Wolfram's Red Salt. On the other hand, the Pt–Pt distance has increased from 5.39 (5) to 5.466 (3) Å. Therefore, this increase is the result of a lengthening of both the Pt(IV)–Cl and the Pt(II)–Cl bond lengths and can be thought of as an increase in the Pt–Pt distance without any change in d.

The spectrum of Wolfram's Red Salt was first reported by Yamada and Tsuchida.[24] In the crystal a single broad band at about $18\,000$ cm^{-1} was observed in the polarization parallel to the stacking direction. Day has reported that the spectrum in this polarization actually consists of a broad band centered at $21\,000$ cm^{-1} with a shoulder at $17\,450$ cm^{-1}.[28] Similar

results were reported by Interante et al.[29] and Clark et al.[30] Clark also reported the resonance Raman spectrum of Wolfram's Red Salt. A long vibrational progression was observed based on a frequency of 319.5 cm^{-1}, which was assigned to the Pt–Cl stretch. From the excitation profile, it was clear that the transition at $17\,450$ cm^{-1} and not the one at $21\,000$ cm^{-1} was responsible for the resonance enhancement. It was proposed, therefore, that the $d_{z^2} \leftarrow d_{z^2}$ transition occurred at $17\,450$ cm^{-1}. This assignment is also consistent with the high-pressure studies on Wolfram's Red Salt done by Interante,[29] which indicated that the shoulder red shifted by ~ 1600 cm^{-1} at a pressure of 30 kbar. This result was based on the assumption of a reduced Pt–Pt distance resulting from the applied external pressure.

The presence of two bands in the spectra of Wolfram's Red Salt complicates assigning the spectrum of $[Pt(NH_3)_4Cl](HSO_4)$. The increase in the Pt–Pt distance will result in a larger d_{z^2}–d_{z^2} separation and should cause this band to blue shift. Therefore, the band $19\,500$ cm^{-1} quite probably represents this transition which has shifted from $17\,450$ cm^{-1} in Wolfram's Red Salt. The question then remains as to what is the band at $21\,000$ cm^{-1} in Wolfram's Red Salt and where is the corresponding band in the tetraammine analogue. Since this transition occurs at an energy lower than any observed in either of the constituent complexes, it must also arise from bands due to the chain structure. It seems unlikely that any such transition should decrease in energy with an increased Pt–Pt distance. The most reasonable solution is that this second transition is also under the broad absorption at $19\,500$ cm^{-1} and was not resolved because of the problems in obtaining the pellet spectrum.

The synthesis of $[Pt(NH_3)_4Cl](HSO_4)_2$ provides insights on why it has proved so difficult to synthesize Wolfram's Red Salt with other amine ligand. The major stabilization in such crystals must be from the band resulting from the overlap of the Pt(IV)–Cl–Pt(II) orbitals. The major factors leading to instability of the chain structure are the electrostatic repulsion of the cationic complexes and any steric hindrance. Indeed, when neutral or single-charged complexes in which there are minimal electrostatic repulsions are stacked, the interactions are a good deal stronger as indicated by the metallic luster and electronic spectrum of these crystals. In these cases the absorption of light polarized parallel to the stacking direction is complete, even in very thin crystals. In the case of stacks composed of dipositively charged cations these interactions are much weaker. This suggests that in Wolfram's Red Salt the stabilization from the formation of the crystal must be only slightly greater than the repulsive electrostatic forces. Changing the ligand to ammonia destroys this balance. The major difference between ammonia and ethylamine is their basicity. Ethylamine is a better base. This means the positive charge on the platinum metal will be lower on the ethylamine complex than on the amine complex. This minor change in the electron density is apparently enough to allow for Wolfram's Red Salt to form as a stable solid. The added stability needed to stabilize the crystals of $[Pt(NH_3)_4Cl](HSO_4)_2$ must come from the extensive hydrogen bonding. This is consistent with the longer Pt–N and Pt–Cl bond lengths observed for $[Pt(NH_3)_4Cl]^{2+}$ as compared to those for $[Pt(NH_2-(C_2H_5))_4Cl]^{2+}$. Hydrogen bonding also explains the synthesis of the previously prepared $[Pt(en)_2Cl](ClO_4)_2$, which has not been structurally characterized. Again, extensive hydrogen bonding between the ligands and the perchlorate anion is expected. In the absence of an anion with oxygens to hydrogen

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bond to, tetraamine complexes with simple amine ligands will be unstable and will not form. In the case of amines with long alkyl groups which are better bases than ethylamine, steric factors account for the instability.

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Magnetic Interactions in Metal Complexes of Pentadentate Binucleating Ligands. 1. Synthesis and Properties of Binuclear Copper(II) Compounds Containing Single-Atom Bridging Ligands. Crystal and Molecular Structure of a Binuclear μ-Hydroxo-Bridged Copper(II) Complex of 1,5-Bis[1-(pyridin-2-yl)ethylideneamino]pentan-3-ol

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A series of binuclear copper(II) complexes based on some new binucleating ligands derived from condensation of salicylaldehyde, pyridine-2-carboxaldehyde, and pyrrole-2-carboxaldehyde with 1,3-diaminopropan-2-ol and 1,5-diaminopentan-3-ol are reported. The compounds feature a bridging ligand alkoxide group and an additional single-atom bridging ligand X (X = OH, OR, Cl, Br). The crystal and molecular structure of the μ-hydroxo-bridged dicopper(II) complex of 1,5-bis[1-pyridin-2-yl)ethylideneamino]pentan-3-ol isolated as the perchlorate salt of formula C₁₇H₂₂N₄O₁₁Cl₂Cu₂ having space group *Pbca* and unit cell dimensions a = 12.287 (14) Å, b = 12.000 (6) Å, and c = 15.487 (8) Å was solved with 2202 nonzero structure factors with $I \geq 2.50(I)$. Refinement by blocked-matrix least-squares methods gave a final R factor of 0.0405. The binucleating nature of the ligand was thus established, the two copper(II) ions being bridged by the secondary alkoxo group of the ligand and an additional hydroxo group. The N₂O₂-donor atom sets around each copper are essentially planar. Both copper atoms may be regarded as having square-pyramidal coordination, one being coordinated to a water molecule and the other having an interaction (Cu–O = 2.234 Å) with the oxygen atom of the bridging OH group of a neighboring binuclear unit. The structure thus involves *pairs of binuclear units*. The intramolecular Cu⋯Cu separation is 2.928 Å. Magnetic susceptibilities of the solid complexes were determined over the temperature range 4.2–300 K. Generally the magnetic behavior conforms closely to the Bleaney–Bowers equation for a spin-coupled $S = \frac{1}{2}$ system in which the singlet–triplet separation is 2J. In some cases a tetramer model was found to give slightly improved fits and yield physically more reasonable g values than were obtained with the Bleaney–Bowers equation. The title compound shows significant intramolecular antiferromagnetic coupling with a best fit J value, –142 cm⁻¹, deduced from both theoretical models. The coupling in the other compounds is shown to be dependent on the nature of the bridging group, the chain length of the ligand backbone, and the extent of saturation of the C–N linkages of the ligands, all of which probably lead to significant structural changes around the copper(II) ions and hence influence the magnetic coupling of the two copper centers. The first examples of ferromagnetic coupling in copper(II) complexes of binucleating ligands of this type are reported.

Introduction

Robson[2] initially designed and synthesised pentadentate binucleating ligands derived from the reaction of 2-aminophenol and 2,6-diformyl-4-methylphenol and isolated complexes of various metals including Cu(II). The formulation **1** featuring a bridging phenoxo group and the additional

1
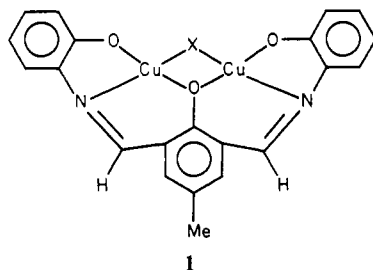
bridging ligand X is now firmly established. The original ligand has been modified extensively,[2–4] and the ligand X may donate one (OR⁻, Cl⁻, etc.) or two (e.g., pyrazolate) atoms to the coordination spheres of the metals.

A number of these binuclear copper(II) species have magnetic properties which indicate considerable antiferromagnetic spin exchange between the copper ($S = \frac{1}{2}$) centers. Variation of the magnitude of this exchange with bridging group X and with the nature of the backbone of the pentadentate ligand has been investigated.[2–4] The occurrence of both antiferromagnetic and ferromagnetic exchange has been noted in a large number of binuclear copper(II) systems,[5–7] but no examples of ferromagnetic coupling have been reported for compounds of the type **1**. Recent studies[8,9] report binuclear

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