

Figure 2. Unit cell diagram for  $\text{WSCl}_4$ . Axes orientation:  $b$ , down;  $c$ , across;  $a$ , toward viewer.

Table III. Least-Squares Planes<sup>a</sup>

atom	$x$	$y$	$z$	dist, Å	esd
Plane 1: $A = 0.3937$ ; $B = 0.8175$ ; $C = -0.4203$ ; $D = -1.0231$					
Atoms in Plane					
Cl(1)	-2.4218	3.8192	7.6101	-0.006	0.011
Cl(2)	-1.6804	5.5469	11.6659	-0.006	0.011
Cl(3)	-0.0412	3.7507	9.6770	0.006	0.012
Cl(4)	-4.0550	5.6528	9.6167	0.006	0.011
$\chi^2 = 1$					
Other Atom					
W(1)	-1.8531	5.0883	9.4376	0.487	0.002
Plane 2: $A = 0.1217$ ; $B = 0.2492$ ; $C = -0.9608$ ; $D = -3.8532$					
Atoms in Plane					
Cl(5)	-5.1864	9.6004	5.0359	0.776	0.010
Cl(6)	-8.0662	8.6010	6.0782	-0.825	0.010
Cl(7)	-3.9291	6.8359	6.1315	-0.812	0.010
Cl(8)	-6.5073	6.5494	3.9898	0.860	0.010
$\chi^2 = 27940$					
Other Atom					
W(2)	-5.8415	7.9671	6.4397	-1.059	0.002

<sup>a</sup>The equation of the plane is of the form  $Ax + By + Cz - D = 0$ , where  $A$ ,  $B$ ,  $C$ , and  $D$  are constants and  $x$ ,  $y$ , and  $z$  are orthogonalized coordinates.

sulfur, the Cl'-W-S angle being  $176.4^\circ$ . The weak tungsten-chlorine interaction occurs across a center of symmetry and results in the formation of dimeric  $\text{W}_2\text{S}_2\text{Cl}_8$  units. These dimers are similar in structure to the isomorphous  $\text{W}_2\text{Cl}_{10}^6$  and  $\text{Mo}_2\text{Cl}_{10}^7$ .

In the new polymorph, we report here there are two  $\text{WSCl}_4$  groups in the asymmetric unit. One of the  $\text{WSCl}_4$  entities (A) relates to its symmetry equivalent across a center of inversion, giving dimeric units of the type just described, while the other  $\text{WSCl}_4$  molecule (B) relieves its nascent coordinative unsaturation by a longer, unreciprocated W(1)-Cl(6) interaction. We will first contrast the dimeric unit in the present compound with that of the triclinic modification.

In the dimeric unit of the present modification, one of the tungsten-chlorine distances, W(2)-Cl(8), is much longer than the other three, 2.433 (12) Å. This lengthening is due to a 2.908 (9) Å interaction between this chlorine atom and the tungsten atom of a symmetry-related (A)- $\text{WSCl}_4$  unit. Furthermore, the W(2)-Cl(8)' distance is 0.14 Å shorter than the analogous interaction in the triclinic modification and the Cl(8)'-W(2)-S(2) angle is  $173.8 (5)^\circ$ . Simultaneously, (A)- $\text{WSCl}_4$  units approach the (B)- $\text{WSCl}_4$  units via a W(1)-Cl(6) contact of 3.233 (11) Å. This contact causes a slight lengthening of the W(2)-Cl(6) bond, which is 2.341 (12) Å. The average W-Cl bond distance for chlorine atoms that do not interact with tungsten atoms is 2.247 [4] Å. The remaining bond distances and angles are normal for this type of distorted-square-pyramidal structure, but they differ considerably from those of the triclinic modification. One manifestation

of these differences is that in the triclinic modification the chlorine atoms were found to be planar with the tungsten atom 0.45 Å above the plane. However, in the present compound the chlorine atoms are far from planar (see Table III).

The five ligands around the tungsten atom in the (B)- $\text{WSCl}_4$  unit form a nearly regular square pyramid. The W-Cl bond lengths and mutually cis Cl-W-Cl and S-W-Cl bond angles are equivalent within experimental error. The four chlorine atoms of the B unit are planar and the tungsten atom sits 0.487 (2) Å above the plane.

The chlorine atoms on the B units do not interact with any other tungsten atoms; hence, tetrameric entities are formed that are internally linked by weak W-Cl bonds. The W(1)-W(2) and W(2)-W(2)' distances are 4.844 (3) and 4.189 (3) Å, respectively, indicating that there is no electronic interaction between the metal centers. Other than the aforementioned contacts, there are no other  $<4.0$  Å contacts between chlorine and sulfur atoms and tungsten atoms on adjacent molecules.

The crystal structure presented here displays a previously unknown mode of association for transition metal oxide/sulfide tetrahalides. The electron deficient and coordinatively unsaturated tungsten atoms of this modification exhibit stabilizing weak W-Cl interactions, which contrasts with the existence of monomeric molecules of  $\text{WOX}_4$  and  $\text{WSX}_4$  in the vapor phase.<sup>8</sup>

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**Registry No.** W, 7440-33-7;  $\text{S}_2\text{Cl}_2$ , 10025-67-9; S, 7704-34-9;  $\text{WSCl}_4$ , 25127-53-1.

**Supplementary Material Available:** Full listings of bond distances, bond angles, and positional and isotropic equivalent displacement parameters for  $\text{WSCl}_4$  (4 pages); a listing of observed and calculated structure factors for  $\text{WSCl}_4$  (6 pages). Ordering information is given on any current masthead page.

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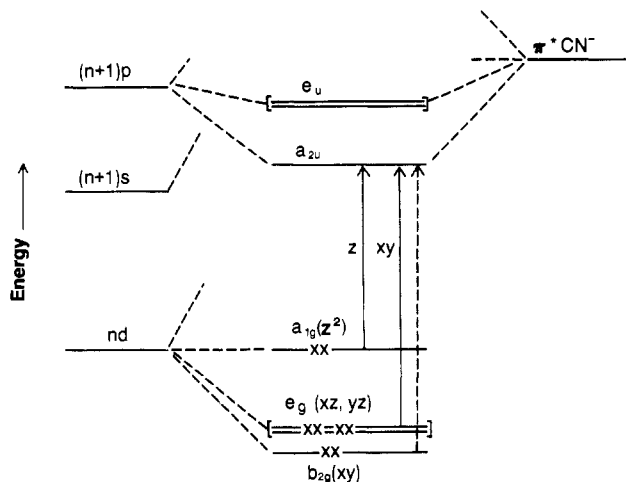
#### Assignment of the Intense UV Bands in the Solution Electronic Spectrum of $\text{Ni}(\text{CN})_4^{2-}$ . MCD Spectra for the 3.7- and 5.0- $\mu\text{m}^{-1}$ Bands

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The intense bands in the region 3.0-4.5  $\mu\text{m}^{-1}$  exhibited by the planar  $\text{Ni}(\text{CN})_4^{2-}$  ion in solutions and in crystalline environments have been investigated by a variety of spectroscopic methods including low-temperature absorption,<sup>1</sup> magnetic circular di-

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**Figure 1.** Relative energy of the spectroscopically important one-electron molecular orbitals for planar  $M(\text{CN})_4^{2-}$ ,  $M = \text{Ni}$  or  $\text{Pt}$  ( $z$  axis is normal to the  $xy$  molecular plane), showing the  $xy$ -polarized  $e_g(xz, yz) \rightarrow a_{2u}$  and  $z$ -polarized  $a_{1g}(z^2) \rightarrow a_{2u}$  excitations. The  $b_{1g}(xy) \rightarrow a_{2u}$  excitation (broken arrow) is forbidden.

chromism (MCD),<sup>2</sup> and polarized single-crystal absorption.<sup>3</sup> These studies have led to assignments based on  $\text{Ni } 3d \rightarrow a_{2u}(\text{Ni } 4p_z, \pi^*(\text{CN}^-))$  excitations (see Figure 1). These assignments have stood for some time and seem to be generally accepted. Further, they parallel  $\text{Pt } 5d \rightarrow a_{2u}(\text{Pt } 6p_z, \pi^*(\text{CN}^-))$  assignments for analogous intense UV bands for the isostructural  $\text{Pt}(\text{CN})_4^{2-}$  ion when differences due to strong  $\text{Pt } 5d$  spin-orbit coupling are taken into account.<sup>2,4</sup> However, recently Arndt, Danielson, Fanta, and Musselman (ADFM)<sup>5</sup> reported polarized specular reflectance spectra for the mixed crystals  $\text{Ba}[\text{Ni}_x\text{Pt}_{1-x}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$  in the region  $3.2\text{--}4.2 \mu\text{m}^{-1}$ , and as a result of their findings, they have proposed new assignments for the  $3.72\text{-}\mu\text{m}^{-1}$  band and a higher energy band system located near  $5.0 \mu\text{m}^{-1}$ . The mixed crystals were prepared by cocrystallization of isomorphous ( $C2/c$ )  $\text{Ba}[\text{Ni}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$  and  $\text{Ba}[\text{Pt}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$  and were assumed to have structures analogous to those of the pure crystals where the metal ions form chains parallel to the  $c$  crystal axis and the molecular planes of the complexes are parallel to one another normal to this axis. The  $M\text{--}M$  distance along the chains was assumed to be in the range  $3.3\text{--}3.4 \text{ \AA}$ , characteristic of the pure crystals.<sup>6,7</sup> The in-plane  $xy$ -polarized spectra derived from the reflectance of the mixed crystals showed two bands: band A, which was composition independent at  $3.53 \pm 0.01 \mu\text{m}^{-1}$ , was attributed to  $\text{Ni}(\text{CN})_4^{2-}$  (aqueous solution band at  $3.72 \mu\text{m}^{-1}$ ), and band B, which varied with composition from  $3.75 \mu\text{m}^{-1}$  (76% Ni, 24% Pt) to  $3.86 \mu\text{m}^{-1}$  (100% Pt), was attributed to  $\text{Pt}(\text{CN})_4^{2-}$  (aqueous solution band at  $3.92 \mu\text{m}^{-1}$ ). The solution bands for both complexes had been assigned earlier to transitions to an  $xy$ -polarized  $E_u$  state derived from the  $e_g(xz, yz) \rightarrow a_{2u}$  excitation.<sup>2,3</sup> ADFM argued that the different composition dependences, together with the observation of two separate bands for Ni and Pt centers in the mixed crystals, implied differing excitations on the two types of metal centers. The lack of composition dependence of the energy for band A was taken to imply that the orbitals of the Ni excited configuration were *not* delocalized and therefore could not involve the out-of-plane  $a_{2u}$  orbital, which is oriented along the metal chain and overlaps strongly with neighboring metal ions. ADFM proposed that band A, and by implication the solution

band at  $3.7 \mu\text{m}^{-1}$ , be assigned to the  $E_u$  state from the  $b_{2g}(xy) \rightarrow e_u(\pi^*(\text{CN}^-))$  excitation, since both orbitals are primarily in-plane and are not expected to be delocalized to any extent. The earlier  $e_g(xz, yz) \rightarrow a_{2u}$  interpretation for the Pt excitation was considered satisfactory, since band B exhibited a small ( $\sim 0.1 \mu\text{m}^{-1}$ ) composition dependence. In this context, it is noteworthy that ADFM base their arguments on an earlier study of the out-of-plane  $z$ -polarized reflectance spectra for the  $\text{Ba}[\text{Ni}_x\text{Pt}_{1-x}(\text{CN})_4] \cdot 4\text{H}_2\text{O}$  crystals.<sup>8</sup> A single intense  $z$ -polarized band was observed, the energy of which showed a large composition dependence from  $2.26 \mu\text{m}^{-1}$  (100% Ni) to  $2.76 \mu\text{m}^{-1}$  (100% Pt), and was significantly red-shifted from the solution positions ( $\text{Ni}(\text{CN})_4^{2-}$ ,  $3.50 \mu\text{m}^{-1}$ ;  $\text{Pt}(\text{CN})_4^{2-}$ ,  $3.92 \mu\text{m}^{-1}$ ). The  $z$ -polarized band was interpreted as the transition to an  $A_{2u}$  excited state resulting from the excitation  $a_{1g}(z^2) \rightarrow a_{2u}$  at both Ni and Pt centers in the crystal. The energy shift and composition dependence were attributed to the delocalization of the  $a_{2u}$  orbitals along the metal chain and to a lesser extent to the delocalization of the  $a_{1g}(z^2)$  orbitals also. Finally after rejecting the  $e_g(xz, yz) \rightarrow a_{2u}$  excitation for band A in the in-plane polarized study, ADFM suggested that this excitation be assigned to a high-energy band near  $5.0 \mu\text{m}^{-1}$  in the solution spectrum of  $\text{Ni}(\text{CN})_4^{2-}$ .

The new assignments proposed by ADFM are difficult to rationalize in view of the earlier MCD results and analysis<sup>2</sup> and provided the motivation for a reinvestigation in our laboratory. MCD measurements have also been extended to include the  $5.0\text{-}\mu\text{m}^{-1}$  band and are reported here in an effort to clarify the assignment of this band.

## Results and Discussion

New MCD measurements at 7-T field strength were made on aqueous solutions of  $\text{K}_2\text{Ni}(\text{CN})_4$  by using a spectrometer and magnet system described earlier,<sup>9</sup> which allows simultaneous and synchronous MCD and absorption determination. The spectrum between  $3.2$  and  $5.4 \mu\text{m}^{-1}$  is presented in Figure 2. The spectrum between  $3.2$  and  $4.5 \mu\text{m}^{-1}$  is in good agreement with the earlier MCD results;<sup>2</sup> the region  $4.5\text{--}5.4 \mu\text{m}^{-1}$  has not been reported previously. It is clear from Figure 2 that there is a strong positive  $A$  term<sup>10</sup> for the  $3.7\text{-}\mu\text{m}^{-1}$  band ( $\bar{A}_1/\bar{D}_0 = +2.1 \pm 0.1$ , by the method of moments;<sup>10</sup> compares favorably with the value  $+2.3$  given earlier<sup>2</sup>) and a weaker negative  $A$  term for the  $5.0\text{-}\mu\text{m}^{-1}$  band ( $\bar{A}_1/\bar{D}_0 = -0.15 \pm 0.03$ ).

The observation of MCD  $A$  terms for both the  $3.7\text{-}$  and  $5.0\text{-}\mu\text{m}^{-1}$  bands is consistent with  $xy$ -polarized transitions to degenerate  $E_u$  states, since the ground state is totally symmetric  ${}^1A_{1g}$ , but the two terms differ in sign and magnitude. The  $A$  term sign and magnitude depend upon the orbitals involved in the transition and for the space-averaged case appropriate for a nonisotropic molecule in solution are given by the  $\bar{A}_1/\bar{D}_0$  parameter ratio in eq 1,<sup>10</sup> where

$$\bar{A}_1/\bar{D}_0 = -\frac{1}{\sqrt{2}\mu_B} \langle E_u || \mu || E_u \rangle \quad (1)$$

$\bar{D}_0$  is the dipole strength of the transition,  $\mu = -\mu_B(L + 2S)$  (the magnetic moment operator), and  $\mu_B$  is the Bohr magneton. For the  $e_g(xz, yz) \rightarrow a_{2u}$  excitation  $\bar{A}_1/\bar{D}_0$  depends upon the magnetic moment of the occupied  $3d_{xz}, 3d_{yz}$  orbitals and is calculated to be  $+1.00$  for pure  $3d$  orbitals.<sup>2,10</sup> In contrast, the  $\bar{A}_1/\bar{D}_0$  value for the  $b_{2g}(xy) \rightarrow e_u$  excitation depends upon the magnetic moment of the  $e_u$  ligand-based orbitals. The calculation of  $\bar{A}_1/\bar{D}_0$  depends upon the exact form of the  $e_u$  orbitals, which is difficult to specify. In the earlier MCD analysis<sup>2</sup> an estimate was made of  $\bar{A}_1/\bar{D}_0 = \sim +0.3$ . Therefore, it appears that the observed  $A$  term for the  $3.7\text{-}\mu\text{m}^{-1}$  band ( $\bar{A}_1/\bar{D}_0 = +2.1\text{--}2.3$ ) is too large for the  $b_{2g}(xy) \rightarrow e_u$  excitation and the  $A$  term for the  $5.0\text{-}\mu\text{m}^{-1}$  band has the wrong sign for the  $e_g(xz, yz) \rightarrow a_{2u}$  excitation. The earlier MCD

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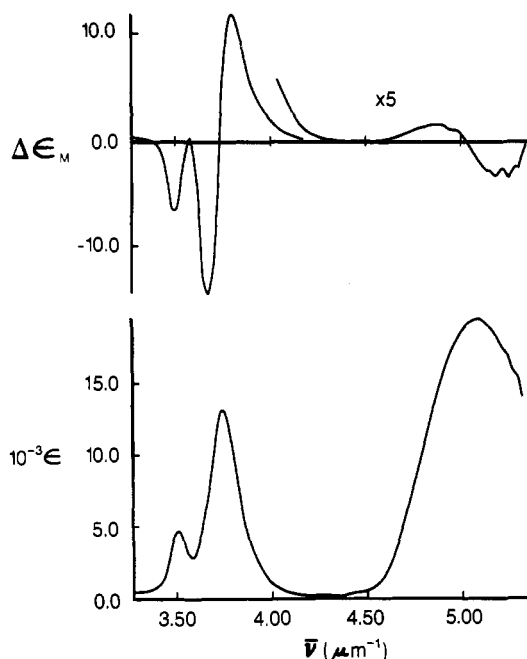
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**Figure 2.** MCD (upper curves) and absorption (lower curve) spectra for aqueous solutions of  $K_2Ni(CN)_4$ . The MCD data between 4.1 and 5.3  $\mu m^{-1}$  were multiplied by a factor of 5 before plotting.

analysis<sup>2</sup> noted that the  $A$  term for the 3.7- $\mu m^{-1}$  band was also larger than could be explained on the basis of the  $3d_{xz}3d_{yz}$  orbitals alone and explained the larger magnitude in terms of a pseudo  $A$  term contribution originating from  $B$  terms of opposite sign for the  $E_u$  state and a neighboring  $A_{2u}$  state at 3.5  $\mu m^{-1}$ , which originates from the  $a_{1g}(z^2) \rightarrow a_{2u}$  excitation. An upper limit of  $A_1/D_0$  was estimated to be +2.6 (see ref 2 for details). Thus, it appears that the earlier interpretation<sup>2</sup> including the pseudo  $A$  term contribution provides a better explanation of the magnitude of the  $A$  term for the 3.7- $\mu m^{-1}$  band than does the ADFM proposal. The negative  $A$  term observed cannot be explained by the ADFM assignment. However, the excitation  $a_{1g}(z^2) \rightarrow e_u$ , which would be expected at slightly higher energies than the  $3d \rightarrow a_{2u}$  excitations, is expected to give an  $A$  term the same in magnitude but opposite in sign compared to the  $A$  term for the  $b_{2g}(xy) \rightarrow e_u$  excitation or  $A_1/D_0 = \sim -0.3$ , on the basis of the earlier estimates.<sup>2</sup> This value compares favorably with the observed value (-0.15). Therefore, the assignment of the 5.0- $\mu m^{-1}$  band to the  $a_{1g}(z^2) \rightarrow e_u$  excitation is proposed here.

In conclusion, the MCD results reported here and earlier<sup>2</sup> are explained easily by the generally accepted  $3d \rightarrow a_{2u}$  assignments for  $Ni(CN)_4^{2-}$ . The new data support the logical extension of these assignments to the higher energy  $e_u$  orbital for the 5.0- $\mu m^{-1}$  band. The ADFM crystal results are not so easily explained, but however they are explained, the solution spectrum is still best interpreted by the conventional excitation scheme.

Registry No.  $Ni(CN)_4^{2-}$ , 48042-08-6.

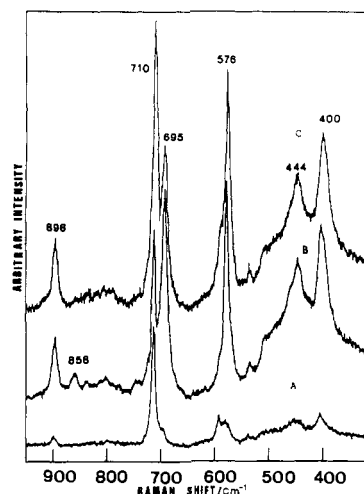
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#### Photochemical Observations in Solutions of Sulfur in Liquid Ammonia

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The photosensitivity of solutions of sulfur in liquid ammonia was first observed by Bernard et al.<sup>1,2</sup> They have shown the



**Figure 1.** Raman spectra of sulfur-ammonia solutions (1 M) recorded with the 514.5-nm excitation line: (A) sample at 223 K recorded just at the beginning of the laser irradiation; (B) sample at 200 K recorded after the laser irradiation had been focused for 2 h on the sample after which the spectrum was then stationary; (C) sample at 223 K recorded after the laser irradiation had been focused for 1 h on the sample after which the spectrum was then stationary.

influence of white-light illumination of the solutions on the absorption spectrum. They have also shown that the photosensitivity could be induced by laser excitation lines (488.0 and 514.5 nm). It was shown that the initial equilibrium state was recovered if the sample was kept for several days in the dark. The experiments of Bernard et al., carried out at room temperature, did not allow identification of the species resulting from the decrease of the  $S_4N^-$  concentration since the spectrophotometry experiments were performed only in the visible range. The observations of Bernard et al. were taken into account in the characterization of the equilibrium state of these solutions.<sup>3,4</sup> Prestel and Schindewolf<sup>5-8</sup> showed that sulfur-ammonia solutions contain several photosensitive species. They established that  $S_3N^-$  or  $S_4N^-$  can be produced through photoinduced reactions.<sup>7,8</sup> However, their experiments did not lead to an overall interpretation of the observed photochemical effects. Furthermore, it was shown recently that the solutions studied by Prestel and Schindewolf were not in the equilibrium state before illumination.<sup>4,9</sup> It is now well established that sulfur in ammonia undergoes a disproportionation process giving  $S_6^{2-}$  in equilibrium with  $S_3^-$  as reduced species and mainly  $S_4N^-$  as oxidized species. In the equilibrium state a large fraction of solubilized sulfur is still in the zero oxidation state.<sup>4,13</sup> This neutral form of sulfur,  $S_{am}$ , is not cyclic  $S_8$ , and likely involves ammonia molecules. For the sake of simplicity we call it  $S_{n,am}$ . We have proposed<sup>4</sup> the following disproportionation equilibrium to describe the equilibrium state, if the concentration of  $S_3N^-$  is neglected:

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