tion of the literature shows that all other reported attempts to prepare hydrogen dihalides from aqueous solutions have also resulted in hydrated products. Curtis[15] examined *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride, prepared from aqueous hydrochloric acid, and its bromide analog; both compounds were dihydrates containing hydrated hydrogen ion and not hydrogen dihalide anion. West[16] reported the preparation of cesium hydrogen dichloride by passing hydrogen chloride into an aqueous solution of cesium chloride, but the product was later shown[17,18] to have a composition corresponding to $(CsCl)(H_3O^+)_{0.75}(Cl^-)_{0.75}$. Schroeder and Ibers[19] have found a second crystalline product in this reaction and have shown by crystallographic analysis that it is $(CsCl)(H_3O^+)_{0.33}(HCl_2^-)_{0.33}$.[20,21] Only in this last compound, where there is an excess of hydrogen halide over water, does a hydrogen dihalide ion appear to exist.

The nature of the hydrated proton is not the same in these salts; X-ray and neutron diffraction studies have shown that $(CsCl)(H_3O^+)_{0.33}(HCl_2^-)_{0.33}$ does contain the hydronium ion,[17,20] while *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride dihydrate and related compounds contain the diaquohydrogen ion, $H_5O_2^+$.[22-25] No structural information is available on West's compound.[15-17] The infrared spectra of the hydrated protons in the tetraphenylarsonium halide hydrohalide dihydrates more nearly resemble that of the diaquohydrogen ion in *trans*-dichlorobis(ethylenediamene)cobalt(III) chloride hydrochloride dihydrate[15] than they do the spectrum of hydronium ion;[26] however, the differences in these spectra are not large enough to allow positive identification by this means. The water in the arsonium hydrates is very tightly held and cannot be removed without concurrent removal of hydrogen halide,[27,28] and the O–H stretching frequencies of the hydrates appear low for a compound containing a molecule of water. This, coupled with the similarities of the stoichiometries of the arsonium and the complex cobalt dihydrates, leads us to suggest that the arsonium hydrates contain the diaquohydrogen ion; however, a final decision would require diffraction studies.

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The Magnetic Circular Dichroism of $Ni(CN)_4^{2-}$

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Received February 2, 1968

The square-planar tetrahalide and cyanide complexes of d^8 transition metal ions show strong absorption bands in the visible–near-ultraviolet spectrum, in addition to the usual weak d → d bands. These have been attributed to intramolecular charge-transfer transitions and detailed assignments were made on the basis of molecular orbital calculations.[3] However, the interpretation is not always unambiguous, and further information on the excited states involved is to be desired. Polarized crystal spectra over a range of temperatures would greatly extend the present knowledge, yielding excited-state symmetries and distinguishing allowed and forbidden transitions. However, as yet, suitable crystals have not been obtained. An alternative tool, and one applicable to solutions, is magnetic circular dichroism (MCD). This likewise enables symmetries of excited states to be elicited; magnetic moments are also accessible and shed additional light on the excited-state wave functions.[4] We have studied the MCD of a variety of d^8 square-planar complexes and here report on $Ni(CN)_4^{2-}$.

A molecular orbital diagram for $Ni(CN)_4^{2-}$, the relevant portion of which is shown in Figure 1, was proposed by Gray and Ballhausen[5] and used to assign the aqueous solution spectrum (Figure 2). Bands 1 and 2 and 3–5 were attributed to d → d and $d \rightarrow \pi^*(a_{2u})$ transitions, respectively. The latter give three singlet states, ${}^1B_{1u}$, ${}^1A_{2u}$, and ${}^1E_u$, arising in turn through excitation of d_{xy}, d_{z^2}, and d_{yz}, d_{xz} electrons. From the ground ${}^1A_{1g}$ state electric dipole transitions are allowed to ${}^1A_{2u}$ and ${}^1E_u$. Band 3, being the weakest of bands 3–5, was therefore assigned to the forbidden ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition. On the basis of the adopted d-orbital order $d_{yz}, d_{xz} < d_{z^2} < d_{xy}$, the upper states of bands 4 and 5 were then taken to be ${}^1A_{2u}$ and ${}^1E_u$, respectively. More recently, Ballhausen and co-workers[6] have reported polarized crystal spectra for a variety of $Ni(CN)_4^{2-}$ salts below 30,000 cm^{-1}. The transitions observed were interpreted as d → d transitions to excited states greatly distorted from planarity.

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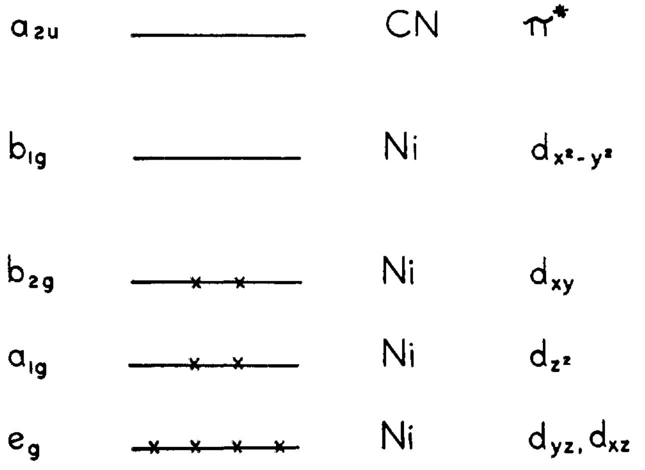

Figure 1.—Portion of Gray–Ballhausen molecular orbital diagram for $Ni(CN)_4^{2-}$. Crosses denote electrons in the ground state.

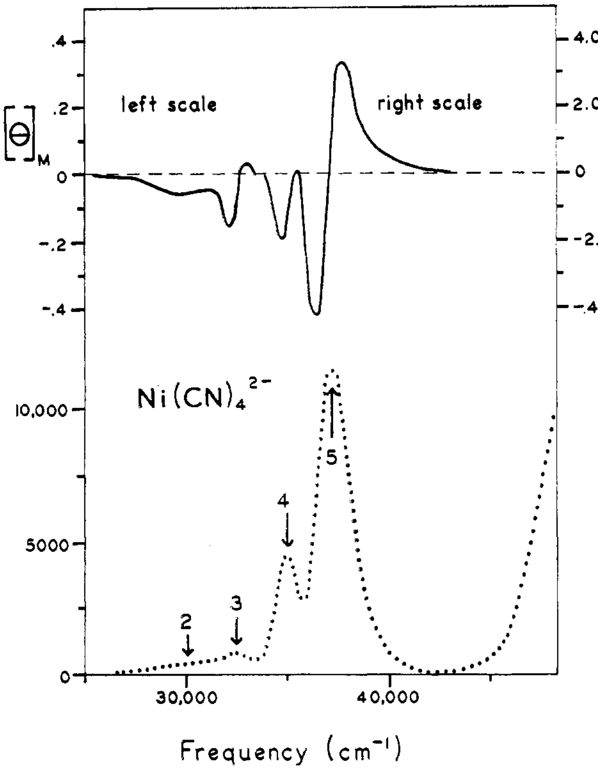

Figure 2.—Absorption spectrum and MCD of $K_2Ni(CN)_4$ in aqueous solution, measured as described in ref 4d. ϵ is the molar extinction coefficient, and $[\theta]_M$ is the molar ellipticity per gauss. Band 1 is reported[5] at 22,500 cm^{-1} and is very weak ($\epsilon \sim 2$). The MCD noise level is negligible.

Since the ground state of $Ni(CN)_4^{2-}$ is electronically nondegenerate, contributions to the MCD of a transition can arise from the magnetic moment of an excited state and from the mixing of different states by the field.[4] The former, called A terms, exhibit a dispersion changing sign through the band and are only present for a degenerate state. The latter, B terms, conversely do not change sign through the band and may occur in nondegenerate transitions. Observation of an A term therefore demonstrates the upper state to be degenerate.

The MCD of $Ni(CN)_4^{2-}$ in aqueous solution is shown in Figure 2. Let us first focus on bands 4 and 5. The clear A term observed in the latter definitely shows the excited state to be degenerate. Within experimental error, only a B term is observed for band 4.[7] The MCD is thus qualitatively consistent with the $^1A_{2u} + {}^1E_u$ excited-state assignments for bands 4 and 5 and hence with the Gray–Ballhausen picture. In addition, it constitutes unambiguous proof—if these are indeed the states present—of the excited-state order $^1A_{2u} < {}^1E_u$. Neither the absorption spectrum nor the theoretical model provided any substantive evidence for this.

Further support for the assignment is obtainable from the sign and magnitude of the A term of band 5. These depend on the magnetic moment of the ^1E_u state. For an $\ldots e_g^4 \rightarrow \ldots e_g^3a_{2u}$ transition, the sole contributor thereto is the e_g level, the a_{2u} orbital having no angular momentum. But the e_g orbitals are close to simple d_{yz}, d_{xz} functions. Their angular momentum and consequently the ^1E_u magnetic moment can therefore be reliably estimated. Assuming pure d functions for the e_g orbitals, we find $\langle {}^1E_ux|\mu_z|{}^1E_uy\rangle = i\beta$, where z is the fourfold molecular axis, ^1E_u x and y functions transform like x and y, $\boldsymbol{\mu} = -\beta(\mathbf{L} + 2\mathbf{S})$ is the magnetic moment operator, and β is the Bohr magneton. The magnitude of the Faraday parameter A[4c,d] can be calculated in terms of $\langle {}^1E_ux|\mu_z|{}^1E_uy\rangle$, and the transition dipole strength D, by methods described previously.[4b,d] The final result is $A/D = \beta/2$. A and D are obtained experimentally by fitting the MCD and absorption spectrum.[4c,d] From Gaussian fits the ratio A/D is found to be 0.8β. The agreement with theory is within the combined uncertainties due to experimental error and the fitting procedures.

The MCD of bands 1 and 2 is uninformative. Band 3 appears to show an A term. If this is genuine and not due to overlapping transitions, the excited state must be degenerate and hence cannot be $^1B_{1u}$. Reassignment is then necessary. Alternative assignment to a d → d transition is unlikely in view of the intensity of band 3, and this applies also to spin-forbidden charge-transfer processes. A spin-allowed charge-transfer transition to another π^* orbital is more consistent with the intensity. However, if other π^* orbitals are in the same region as $a_{2u}(\pi^*)$, more than three d → π^* bands would be expected. The possibility that the charge-transfer bands are ligand to metal and not metal to ligand has been suggested by Jørgensen.[8] However, the dissimilarity of both absorption spectrum and MCD from those of the square-planar halides[3,9] militates against this. Lastly, it might be that, as in the d → d transitions,[6] the use of D_{4h} is not appropriate. In this case, a completely new spectral interpretation would be called for. Alternatively, band 3 may be

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(7) The MCD actually appears to cross the axis (and thus change sign) at the high-frequency end of band 4, but the effect is so small as to be within the experimental uncertainty of the data.

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composite, containing, for example, a high-energy d → d transition and the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition. Further study of this transition is clearly necessary.

We conclude that the MCD of bands 4 and 5 fits nicely with Gray and Ballhausen's assignments, but we have no detailed explanation for the behavior of band 3.

Acknowledgment.—This work was supported in part by a grant from the National Science Foundation.

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Organotellurium, -selenium, and -sulfur Derivatives of π-Cyclopentadienylmolybdenum Tricarbonyl

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Received March 8, 1968

The donor properties of most of the heavier elements of groups IVa, Va, and VIa of the periodic table toward transitional metal substrates have been investigated a great deal in the past decade. However, little interest in the donor properties of tellurium has been shown, as evidenced by the fact that only a dozen or so complexes containing transitional metal–tellurium bonds have been described in the literature.[3]

We have, in this laboratory, commenced an investigation of the donor properties of tellurium in transitional metal complexes, and report herein results obtained for the reactions of diphenyl ditelluride, and the analogous selenium and sulfur compounds, with π-cyclopentadienylmolybdenum tricarbonyl dimer.

Experimental Section

I. **Materials.**—All reactions and work-ups were performed in a nitrogen atmosphere. Solvents were degassed with nitrogen prior to use.

Cyclopentadienylmolybdenum tricarbonyl dimer was prepared by a literature method.[4] Diphenyl disulfide, diphenyl diselenide, and diphenyl ditelluride were obtained from commercial sources and used without further purification. Merck acid-washed alumina was used for chromatography.

II. **Reactions of $(C_6H_5)_2Te_2$ with $[\pi\text{-CpMo(CO)}_3]_2$. (A) Preparation of $\pi\text{-CpMo(CO)}_3TeC_6H_5$.**—Diphenyl ditelluride (0.63 g, 1.5 mmol), $[\pi\text{-CpMo(CO)}_3]_2$ (0.73 g, 1.5 mmol), and benzene (100 ml) were placed in a reaction flask which was maintained at 25° with a water bath. The mixture was stirred for 3 hr and irradiated during this period with a 250-W infrared heating lamp. The violet solution was filtered, and solvent was removed under reduced pressure from the filtrate to yield a dark, gummy solid. Recrystallization from benzene–hexane gave dark violet, air-stable crystals, mp 80–82° dec. *Anal.* Calcd for $C_{14}H_{10}O_3TeMo$: C, 37.39; H, 2.24; mol wt, 450. Found: C, 38.18; H, 2.62; mol wt, 500. Attempts to purify the compound by sublimation resulted in decomposition to $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$. Mononuclear $\pi\text{-CpMo(CO)}_3TeC_6H_5$ is soluble in benzene, CS_2, and $CHCl_3$. Solutions of the complex undergo slow decomposition in a nitrogen atmosphere at room temperature. The infrared spectrum[5] of a CS_2 solution of the complex includes bands at 2016 (vs, sp), 1948 (sh), and 1937 (vs) cm^{-1}. The proton nmr spectrum includes a singlet at τ 4.72 due to the cyclopentadienyl protons and a complicated phenyl-hydrogen resonance with a 1:1 ratio of cyclopentadienyl to phenyl hydrogens.

(B) **Preparation of $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$.**—Diphenyl ditelluride (1.15 g, 2.8 mmol) and $[\pi\text{-CpMo(CO)}_3]_2$ (1.25 g, 2.5 mmol) were added to 100 ml of benzene and the mixture was refluxed for 14 hr to give a dark brown solution. After the mixture had cooled, it was filtered, and the filtrate was taken to near dryness, resulting in a dark brown, gummy solid. This material was dissolved in a small amount of benzene, hexane was added, and dark brown crystals formed as the solvent slowly evaporated in a stream of nitrogen. The crystals, which are stable in air and melt at 175–176°, were obtained in 80% yield. *Anal.* Calcd for $C_{26}H_{20}O_4Te_2Mo_2$: C, 37.02; H, 2.39; Te, 30.25; Mo, 22.75; mol wt, 843. Found: C, 37.14; H, 2.49; Te, 31.16; Mo, 23.37; mol wt, 840. The dinuclear compound $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$ is soluble in aromatic hydrocarbons, carbon disulfide, and chloroform, but only sparingly soluble in hexane. Solutions of the complex are slightly air sensitive and deposit a fine, black precipitate. The infrared spectrum in CS_2 includes bands at 1960 (s), 1935 (vs), 1876 (vs), and 1860 (s) cm^{-1} in the carbonyl stretching region. The ^1H nmr spectrum shows a singlet at τ 4.88 in addition to the phenyl multiplet.

(C) **Preparation of $[\pi\text{-CpMo(TeC}_6H_5)_2]_x$.**—Diphenyl ditelluride (0.5 g, 1.2 mmol) and $[\pi\text{-CpMo(CO)}_2TeC_6H_5]_2$ (1 g, 1 mmol) were added to 100 ml of xylene and the mixture was refluxed for 5 hr. After the solution had cooled, the dark brown solid which had formed was collected on a filter and washed with hexane. The yield of the amorphous solid was 0.6 g. *Anal.* Calcd for $C_{17}H_{15}Te_2Mo$: C, 35.79; H, 2.65; Mo, 16.82. Found: C, 35.52; H, 2.91; Mo, 16.30. An infrared spectrum of a Nujol mull of the solid showed no absorptions in the 1700–2200-cm^{-1} region. The material is very insoluble in organic solvents and water, is not volatile, and decomposes at temperatures greater than 190°. A molecular weight measurement was not possible owing to the insoluble nature of the compound.

III. **Reactions of $(C_6H_5)_2Se_2$ with $[\pi\text{-CpMo(CO)}_3]_2$. (A) Preparation of $\pi\text{-CpMo(CO)}_3SeC_6H_5$.**—Diphenyl diselenide (0.5 g, 1.6 mmol) and $[\pi\text{-CpMo(CO)}_3]_2$ (0.79 g, 1.6 mmol) were added to 100 ml of benzene, and the reaction mixture was maintained at 10° with an ice–water bath. The mixture was stirred, and samples were removed periodically to record an infrared spectrum. After 2 hr of stirring, an infrared spectrum indicated that the principal carbonyl-containing species in solution was a material analogous to mononuclear $\pi\text{-CpMo(CO)}_3TeC_6H_5$. The reaction mixture was then filtered, and the filtrate was taken to dryness under reduced pressure, yielding a red solid which had a tendency to change to an oil. The material, which from its infrared spectrum appeared to be a mixture of $\pi\text{-CpMo(CO)}_3SeC_6H_5$ and $[\pi\text{-CpMo(CO)}_2SeC_6H_5]_2$, was dissolved in toluene and the solution was chromatographed on a 50-cm alumina column by elution with a 2:1 mixture of hexane and toluene. A partial separation of the compounds was achieved as a band developed whose upper por-

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