bands of PMT. An alternative possibility for the 281-cm^{-1} band is the metal–ligand asymmetric stretch. The 198-cm^{-1} band probably corresponds to the metal–ligand deformation mode.

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The Configuration of Bis(N-dimethylamino)tetrachlorotriphosphonitrile

BY C. T. FORD, F. E. DICKSON, AND I. I. BEZMAN

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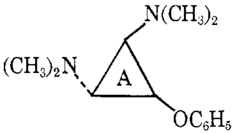
Three forms of the compound $P_3N_3Cl_4[N(CH_3)_2]_2$ have been reported, melting at 103,[1] 82,[2] and 62°.[2] The first of these, I, is formed predominantly and we reported previously[3] that it was a nongeminal *cis* isomer. This conclusion was drawn from the reaction sequence

$$\underset{}{\text{I}} \xrightarrow[AlCl_3]{C_6H_6} \underset{\text{II}}{P_3N_3(Cl)_2(C_6H_5)_2[N(CH_3)_2]_2} \xrightarrow{(CH_3)_2NH(g)} \underset{\text{III}}{P_3N_3(C_6H_5)_2[N(CH_3)_2]_4}$$

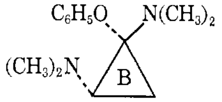
and the knowledge, from proton magnetic resonance measurements, that, in III, two $[N(CH_3)_2]$ groups are attached to the same phosphorus and the other two to separate phosphorus atoms and are *cis* to each other. In II, the spectra showed that the $[N(CH_3)_2]$ groups are each on a phosphorus atom to which a phenyl group is also attached. It was also based on the assumption that no isomerization takes place during the reactions. Since our report, two papers[2,4] have appeared in which evidence was given that I is the *trans* isomer. Further, there have appeared reports of isomerization of aminophosphonitriles in the presence of $AlCl_3$[5] or of amine hydrochlorides.[6] We, therefore, reinvestigated the structure of I and found other evidence that it is, indeed, the *trans* rather than the *cis* isomer.

This was obtained by proton nmr measurements for $P_3N_3Cl_3[N(CH_3)_2]_2(OC_6H_5)$, IV, mp 55°, which was prepared in 95% yield by the action of KOC_6H_5 on I (1:1 mole ratio) in refluxing benzene.

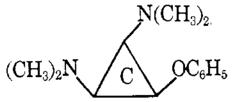
There are six possible configurations for IV as shown below. The apices of the triangles represent the phosphorus atoms in the ring. Given below each structure are the anticipated pmr spectral characteristics. The apparent[3] coupling constant, J'_{PH}, values are in cps.



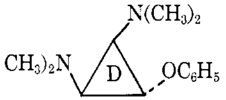
2 doublets
$J'_{PH} = 17.5$ for each



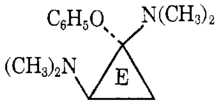
2 doublets
$J'_{PH} = 17.5, 12.5$



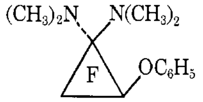
1 doublet
$J'_{PH} = 17.5$



1 doublet
$J'_{PH} = 17.5$



2 doublets
$J'_{PH} = 17.5, 12.5$



2 doublets
$J'_{PH} = 11.6$ for each

Proton nmr spectra were obtained for compound IV on a Varian A-60 nmr spectrometer system operating at 60 Mc/sec with tetramethylsilane employed as an internal reference. Samples were prepared as 20% solutions (w/v) in $CDCl_3$. The spectrum showed two distinct doublets, each having a J'_{PH} = 17.5 cps. This is uniquely characteristic of structure A.

It now appears that Friedel-Crafts phenylation of I to give II is accompanied by isomerization of the $N(CH_3)_2$ groups to the *cis* configuration, the effective agent being $AlCl_3$. Although isomerization probably was not complete, the yield of II, 38%, indicates that the *cis* isomer was more amenable to isolation under the conditions used.

Acknowledgment.—This work was carried out for the Armstrong Cork Co., Lancaster, Pa., to whom we are indebted for long-term financial support.

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(3) C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, **3**, 177 (1964).
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The 20°K Spectrum of Sodium Thiochromite

BY S. L. HOLT AND A. WOLD

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There has been much interest in recent years in the spectra of transition metal compounds in which the ligand field is essentially octahedral but possesses a small trigonal distortion.[1–3] Attempts have been made to determine the source of band intensity and the

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(1) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **33**, 1208 (1960).
(2) D. S. McClure, *ibid.*, **36**, 2757 (1962).
(3) R. M. McFarlane, *ibid.*, **39**, 3118 (1963).

magnitude of the noncubic component of the ligand field in various complexes. None of this work has produced any reliable data involving a transition metal ion in a trigonally distorted sulfide ligand field, however. Consequently, we wish to report on the low-temperature spectrum of sodium thiochromite.

$NaCrS_2$ crystallizes in the space group $R\bar{3}m$. Each chromium ion lies on a site of $\bar{3}m$ symmetry and is surrounded by six sulfide ions at a distance of 2.44 A.[4] Deviation from octahedral symmetry is accomplished by a compression along the trigonal axis.

Experimental Section

Single crystals of $NaCrS_2$ were obtained as hexagonal plates by a procedure similar to the one described in Brauer's handbook.[5] Three grams of potassium chromate, 90 g of potassium sodium carbonate, and 90 g of sulfur were intimately mixed and placed in a covered glazed porcelain crucible. The mixture was heated from room temperature to 850° over a period of 7 hr and allowed to remain at 850° for 1 hr. The sample was then cooled slowly overnight and the cooled unit was transferred to a 2-l. beaker containing 1000 ml of water. After all of the soluble salts were dissolved, the residue was filtered off and washed thoroughly with a dilute alcoholic sodium hydroxide solution, then with pure alcohol, and finally with acetone.

The product appeared as well-formed gray-black hexagonal leaflets by reflected light and garnet red by transmitted light. X-Ray and chemical analysis showed that the crystals were homogeneous and corresponded to the formula $NaCrS_2$. The product contained no potassium despite the use of potassium-containing starting materials.

The growth habit of this material, *i.e.*, (001) face predominant, allowed measurement of the axial spectrum. Attempts to produce crystals where the (100) face was developed, in order to measure the orthoaxial (σ, π) spectra, were not successful.

The axial spectrum was recorded using a Cary 14 spectrophotometer. Samples were cooled by conduction using a Cryo-Tip liquid hydrogen cryostat. A typical crystal used for these experiments was 5 mm across and 0.0025 mm thick.

The spectra of $NaCrS_2$ at 300 and at 20°K are displayed in Figure 1; band maxima and extinction coefficients are collected in Table I. Molar extinction coefficients are probably correct to only ±15% owing to a similar inaccuracy in the thickness measurement.

Discussion

As is shown in Figure 1 we were unable to record the single-crystal spectrum of $NaCrS_2$ beyond 18,500 cm^{-1} owing to the relatively high extinction coefficient of the absorption bands in the blue. Attempts were made to alleviate this situation by pressing the sulfide into KBr and NaCl pellets and by preparation of various mulls. This did not succeed. However, important information can be obtained from that part of the spectrum which we have measured.

In an octahedral field the ^4F term (it is unnecessary for our purposes to consider the higher ^4P term) of the d^3 configuration splits into a low-lying $^4A_{2g}$ and higher lying $^4T_{2g}$ and $^4T_{1g}$ terms. This is shown in Figure 2 along with the magnitude of the splittings in the strong-field limit. Under the influence of the D_{3d} site symmetry the $^4T_{2g}$ level splits into a ^4E_g and a $^4A_{1g}$ component while the $^4T_{1g}$ term splits into ^4E_g and $^4A_{2g}$ components. The $^4A_{2g}$ ground state remains unsplit.

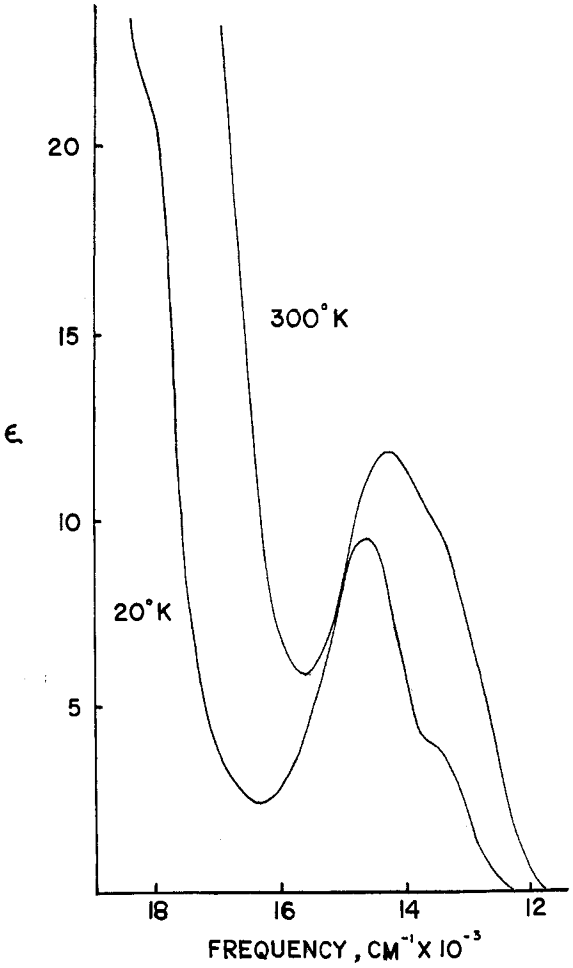

Figure 1.—Spectrum of $NaCrS_2$ at 300 and 20°K.

TABLE I

SUMMARY OF SPECTRAL PARAMETERS FOR $NaCrS_2$ AT 20°K

Transition	ν_{max}, cm^{-1}	ϵ_{max}	f	v, cm^{-1}
$^4A_{2g} \rightarrow {}^4T_{2g}$	13,350	3.2	1.17×10^{-5}	2500
	14,600	9.8	6.63×10^{-5}	
$^4A_{2g} \rightarrow {}^4T_{1g}$	18,000	Sh		
	19,250[a]			

[a] ν_{max} estimated from 18,000 + (v/2).

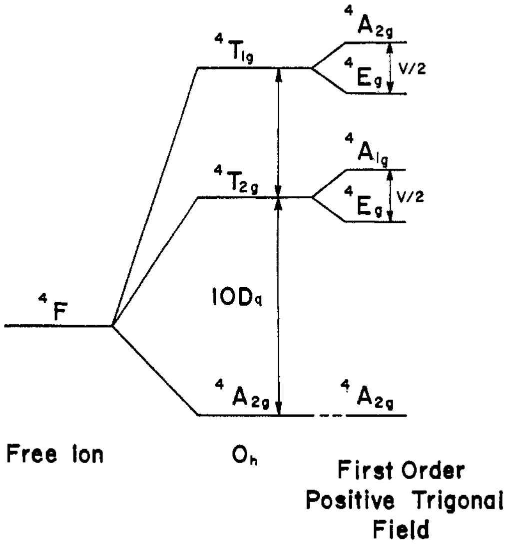

Figure 2.—Energy level diagram for chromium(III) in octahedral and trigonal fields.

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(4) J. W. Boon and C. H. MacGillavry, *Rec. Trav. Chim.*, **61**, 910 (1942).

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The separation of the ^{4}A and ^{4}E components of the ^{4}T states may be expressed in terms of the first-order trigonal field parameter, v, as $v/2$.[6] Assuming that the peaks at 13,350 and 14,600 cm^{-1} are the trigonal components of the $^4T_{2g}$ term, we may calculate v to be 2500 cm^{-1}. It is not possible to obtain the sign of the trigonal field as all of the transitions in question are vibronically allowed in D_{3d} symmetry. (The shift by the absorption maxima toward the blue region of the spectrum and the accompanying decrease in over-all intensity with decreasing temperature clearly demonstrate the vibronic nature of the intensity mechanism.)

If, however, we look at the absolute value of the trigonal field, $|v|$, we see that the axial distortion in $NaCrS_2$ ($|v| = 2500$) is much larger than in Cr_2O_3 ($|v| = 700$)[7] or even in ruby ($|v| = 1425$)[6] where the Cr^{3+} ion finds itself in a site which is ~0.1 A too small for it.

If only a first-order trigonal field is active, the center of gravity of the $^4T_{2g}$ level is maintained and we may calculate a value for Dq. Since the energy of the transition $^4A_{2g} \rightarrow {}^4T_{2g}$ is equal to $10Dq$ we find that for $NaCrS_2$ Dq is 1400 cm^{-1}. Further, if the shoulder at ~18,000 cm^{-1} is taken as the lower trigonal component of the $^4A_{2g} \rightarrow {}^4T_{1g}$ transition, we may calculate, using the strong-field matrix[8] for $^4T_1$ and a value of 18,625 cm^{-1} ($18{,}000 + (v/4)$) for $E(^4A_1 \rightarrow {}^4T_1)$, the value of the Racah parameter B to be 440 cm^{-1}. Since the free-ion value, B_0, for Cr^{3+} is 918 cm^{-1},[9] we may estimate the nephelauxetic ratio β ($B/B_0 = \beta$) for $NaCrS_2$ to be 0.480, a value which is nearly the same as the $\beta = 0.484$ reported by Companion and Mackin.[10]

Using the data of McClure, which were also obtained by single-crystal methods, we find for Cr_2O_3 $B = 503$ cm^{-1} and $\beta = 0.549$. Contrary to Companion and Mackin,[10] we feel this indicates a real difference between the degree of covalence in the Cr–O and Cr–S bonds in Cr_2O_3 and $NaCrS_2$.

Acknowledgment.—Thanks are due to R. A. Palmer for helpful discussion.

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(7) D. S. McClure, *ibid.*, **38**, 2289 (1963).

(8) D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals," Academic Press Inc., New York, N. Y., 1959.

(9) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Inc., New York, N. Y., 1962, Table 16.

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Solution Properties of Some Hexafluorides in Anhydrous Hydrogen Fluoride[1,2]

By Boris Frlec[3] and Herbert H. Hyman

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A long-standing interest in hexafluorides has been stimulated recently by the most interesting properties of xenon hexafluoride. Among the more surprising chemical properties of this compound are the extensive solubility in anhydrous hydrogen fluoride and the high electrical conductivity of the resulting solutions.[4]

Among the hexafluorides, xenon hexafluoride is the clear exception. Stable hexafluorides are expected to dissolve in liquid hydrogen fluoride without fluoride ion transfer,[5] because of the geometrical stabilization of the octahedrally symmetrical compounds. With a few exceptions, however, systematic studies of dilute solutions in hydrogen fluoride have not been reported, even if we include studies of the octahedral hexafluoro anions.[6,7]

In the present work, the electrical conductivities and Raman spectra of solutions of molybdenum, tungsten, uranium, rhenium, and osmium hexafluorides in hydrogen fluoride were investigated in order to determine the degree of ionization of these compounds in such solutions. The solubilities were also determined.

Hydrogen fluoride absorbs in the infrared and the absorption is quite intense in the region near 600 cm^{-1} where many metal–fluorine vibration bands are observed. But the Raman spectrum can be observed without interference and for the highly symmetrical hexafluoride molecules the Raman spectrum is striking.

Results are presented in Tables I–III.

TABLE I

THE SOLUBILITY OF SOME HEXAFLUORIDES IN ANHYDROUS HYDROGEN FLUORIDE AT ROOM TEMPERATURE

MF_6	Moles of MF_6/1000 g of HF
MoF_6	1.50
WF_6	3.14
UF_6[a]	0.49
ReF_6	1.75
OsF_6[b]	0.97
XeF_6[c]	8.6

[a] G. P. Rutledge, R. L. Jarry, and W. Davis, Jr., *J. Phys. Chem.*, **57**, 541 (1953). [b] Value may be affected by reaction with container, see text. [c] Ref 4.

Experimental Section

Materials.—Hydrogen fluoride with a specific conductivity of 10^{-5}–10^{-6} ohm^{-1} cm^{-1} at 0° was prepared by fractional distillation as described elsewhere.[8] Uranium hexafluoride (Oak Ridge National Laboratory) and tungsten and molybdenum hexafluorides (General Chemical Division of Allied Chemical Corp., high purity material) were additionally purified by repeated pumping off of any hydrogen fluoride impurity at −78°.[9] Rhenium

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Paper presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(3) On leave from Nuclear Institute, "Josef Stefan," Ljubljana, Yugoslavia.

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