

by Simmons.^{20,25} This dicobalt(II) heteropoly anion reacts in solution with acid, quantitatively with respect to the W atoms, to produce the $[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$ ion and hydrated cobalt(II) ions.²⁰ The spectrum of such a solution was first reported by Simmons²⁰ and it is shown as curve C in Figure 4. As expected curve C is almost identical with that obtained with a solution of $\text{K}_6[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]$ which is reproduced as curve D. When solutions of $\text{Na}_{6.8}[\text{H}_{0.2}(\text{H}_2\text{O})\text{Co}^{2+}\text{O}_5\text{GaO}_4\text{W}_{11}\text{O}_{30}]$ are acidified at room temperature (to pH of 0.8) the absorbance in the 500–700-nm region begins to decrease rapidly. The curves are identical with curve A in Figure 4, except for a shift to shorter wavelengths of approximately 25 nm. And, at no time, is there evidence for formation of the $[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$ ion, by either spectra or color. This ion is therefore not one of the products when cobalto(II)undecatungstogallate(III) reacts with acid.

The near-infrared spectra for $1.00 \times 10^{-2} M$ solutions of $\text{Ba}_3[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]$ and $\text{K}_6[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]$ are shown as Figure 5. The curves are essentially the same and they correspond to the spectrum of this heteropoly anion, and of Co(II) ions in a weak tetrahedral field, as reported by Simmons.^{20,25} There was no appreciable absorption by solutions of $\text{Na}_{6.8}[\text{H}_{0.2}(\text{H}_2\text{O})\text{Co}^{2+}\text{O}_5\text{GaO}_4\text{W}_{11}\text{O}_{30}]$ in the 1000–2000-nm range, even for solutions as concentrated as $6.0 \times 10^{-2} M$. This study therefore supports the visible spectral study.

Additional information relative to the octahedral coordination of cobalt(II) in the cobalto(II)undecatungstogallate(III) complex is afforded by the red (pink) color of the heteropoly anion since this is a characteristic color for cobalt(II) in octahedral coordination.²⁰ The blue color of the $[\text{Co}^{2+}\text{O}_4\text{W}_{12}\text{O}_{36}]^{6-}$ ion is characteristic for cobalt(II) in tetrahedral coordination.

The X-ray powder pattern of ammonium sodium cobalto(II)undecatungstogallate(III) was compared to a pattern of ammonium sodium undecatungstogallate(III), $(\text{NH}_4)_7\text{Na}_2[\text{H}_2\text{GaO}_4\text{W}_{11}\text{O}_{36}] \cdot 15\text{H}_2\text{O}$, which was taken on the same instrument at 26.0° .²⁶ Although the crystallographic unit cell edges are slightly different, being 22.42 and 21.12 Å, respectively, there was excellent agreement between both line positions and intensities. There were no lines corresponding to those impossible combinations of $h^2 + k^2 + l^2$ for the cubic system. Ammonium sodium cobalto(II)undecatungstogallate(III) is thus a new isomorph of that series of heteropoly tungstates possessing Keggin-type anions.^{1,2,7}

Single-crystal X-ray structural work with ammonium sodium undecatungstogallate(III)³ and other of its isomorphs^{1,2} have shown that the possible space groups are $Fm\bar{3}m$, $F\bar{4}3m$, $F432$, or $F23$. Each of these requires 8 ions, with the characteristic four three-fold axes of symmetry of a Keggin-type anion, in its crystallographic unit cell. Our experimental value of 8.01, for the number of formula weights of ammonium sodium cobalto(II)undecatungstogallate(III) in its crys-

tallographic unit cell, is thus in excellent accord with the aforementioned requirement.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WYOMING, LARAMIE, WYOMING 82070

The 5° Crystal Spectra of Nickel(II) Chloride and Nickel(II) Bromide¹

By J. ACKERMAN, C. FOUASSIER,² E. M. HOLT, AND S. L. HOLT*

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The optical properties of magnetically concentrated systems have generated much interest in recent times. Principally, investigations have centered around the observation of magnon side bands.^{3–5} The most common type of system on which these investigations have been carried out is that in which antiferromagnetic coupling occurs. NiCl_2 and NiBr_2 are examples of a somewhat different magnetic system; both are metamagnets. In these compounds layers of ferromagnetically coupled ions are coupled together antiferromagnetically. NiCl_2 has a $T_n = 50^\circ\text{K}$ ⁶ while NiBr_2 has a $T_n = 60^\circ\text{K}$.⁷ Since these temperatures are within range of normal cryogenic techniques, both systems provide us an opportunity to investigate the possible optical manifestation of cooperative effects in metamagnetic compounds.

Experimental Section

Crystals of NiCl_2 and NiBr_2 were grown by vapor transport using H_2O as the transporting agent. While this technique provided crystals of excellent optical quality, the only growth habit which was found was that with the (001) face prominent. This allowed the measurement of the axial spectrum only. Typical crystal dimensions were $5 \times 5 \times 0.15$ mm.

Crystals of Ni^{2+} in CdCl_2 and CdBr_2 were prepared by the Bridgman technique. The spectra of these materials were also measured with the incident radiation parallel to the c -axis crystal directions and faces were identified using precession and Weissenberg techniques.

Optical measurements were made using a Cary 14R spectrophotometer. Sample temperatures of 298, 80, and 5°K were obtained by previously reported techniques.^{8–10} For temperatures of 113 and 195°K , isopentane and Dry Ice–acetone slushes were used.

Crystal Structures

NiCl_2 and NiBr_2 have the CdCl_2 and CdBr_2 struc-

(1) Supported by NSF Grants GP15432 and GP15432 A1, the Research Corp., and the Office of Naval Research.

(2) On leave from the University of Bordeaux.

(3) D. D. Sell, *J. Appl. Phys.*, **39**, 1030 (1968), and references therein.

(4) M. Kozielski, I. Pollini, and G. Spinolo, *Phys. Rev. Lett.*, **27**, 1223 (1971), and references therein.

(5) C. Simo and S. L. Holt, *J. Solid State Chem.*, **4**, 76 (1972), and references therein.

(6) M. E. Lines, *Phys. Rev.*, **131**, 546 (1963).

(7) I. Tsubokawa, *J. Phys. Soc. Jap.*, **15**, 2109 (1960).

(8) C. Simo and S. L. Holt, *Inorg. Chem.*, **7**, 2655 (1968).

(9) C. Simo, E. Banks, and S. L. Holt, *ibid.*, **9**, 183 (1970).

(10) J. Milstein and S. L. Holt, *ibid.*, **8**, 1021 (1969).

(25) V. E. Simmons, *Proc. Int. Conf. Coord. Chem.*, **7**, 195 (1962).

(26) The temperature of the measurement is given because Baker and we discovered and reported that ammonium sodium undecatungstogallate(III) displays continuous, rapid, reversible, and appreciable shrinkage of its crystallographic unit cell on being heated through the temperature range 25 – 40° . See L. C. W. Baker, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2329 (1966), and also *Chem. Eng. News*, **44**, 44 (1966).

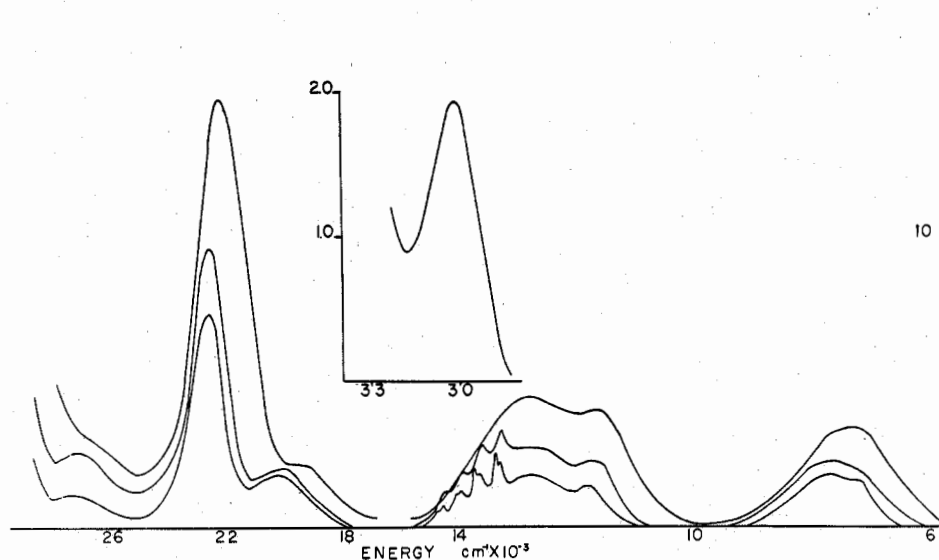


Figure 1.—The electronic spectrum of NiCl_2 ; upper trace, 300°K ; middle trace, 80°K ; lower trace, 5°K .

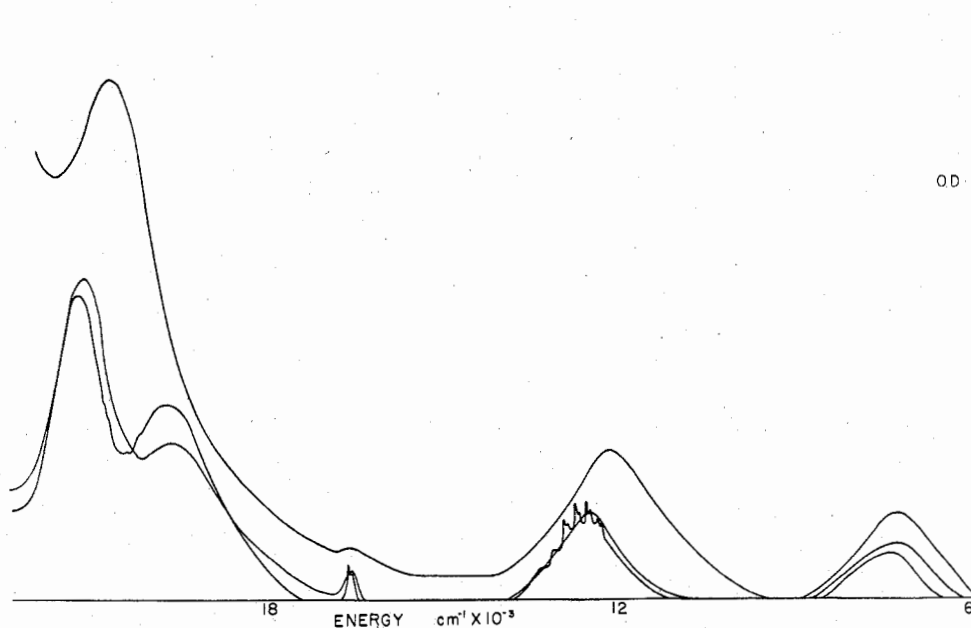


Figure 2.—The electronic spectrum of NiBr_2 : upper trace, 300°K ; middle trace, 80°K ; lower trace, 5°K .

tures, respectively,¹¹ crystallizing in the space group $R\bar{3}m$. Each metal ion is at the center of symmetry of a trigonally distorted octahedron of Cl^- ions. The threefold axes of the molecules are normal to the (001) crystal face.

Results

The absorption spectra of NiCl_2 and NiBr_2 taken at 300, 80, and 5°K are shown in Figures 1 and 2. The spectra of $\text{CdCl}_2\text{-Ni}^{2+}$ and $\text{CdBr}_2\text{-Ni}^{2+}$ taken at 5°K are shown in Figure 3. Figure 4 displays the $30,000\text{-cm}^{-1}$ region of the NiCl_2 spectrum taken at 80, 113, and 195°K . Tables I and II contain a compilation of the band maxima in the 5°K spectra and a comparison of calculated and observed energies for the various Ni^{2+} compounds. Calculations were made using the

matrices of Liehr and Ballhausen¹² incorporated into a program written in our laboratories. The energies quoted for the sharper maxima are accurate to $\pm 10\text{ cm}^{-1}$ while the accuracy of the energies quoted for the broader bands is closer to $\pm 100\text{ cm}^{-1}$. Table III gives the variation of oscillator strength of pertinent maxima as a function of temperature and concentration.

Referring to Figure 1, it can be seen that the broad maxima which are found in the energy ranges, $6000\text{--}9000$, $10,000\text{--}15,000$, and $21,000\text{--}24,000\text{ cm}^{-1}$ decrease in intensity and shift toward the blue end of the spectrum as the temperature is lowered. The broad maximum at $20,000\text{ cm}^{-1}$ has a fairly constant integrated intensity however. In addition certain other features appear at low temperatures. These include the relatively sharp double progression which commences at

(11) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962.

(12) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (New York)*, **6**, 134 (1959).

TABLE I
 OBSERVED ENERGIES (IN cm^{-1}) IN THE 5°K ABSORPTION SPECTRA OF NiCl_2 AND $\text{CdCl}_2\text{-Ni}^{2+}$

NiCl_2			$\text{CdCl}_2\text{-Ni}^{2+}$				
Obsd		Calcd ^a		Obsd	Calcd ^b	Assignment	
E	ΔE	E	Assignment	E	ΔE	E	
7,697		7,720	${}^3A_{2g} \rightarrow {}^3T_{2g}$	7,200		7,222	${}^3A_{2g} \rightarrow {}^3T_{2g}$
11,850		12,400	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$	11,365		11,833	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$
12,700				12,920	-290	13,147	${}^3A_{2g} \rightarrow {}^1E_g$
13,324	-337			13,210		19,291	${}^3A_{2g} \rightarrow {}^1A_{1g}$
13,405				19,200	21,351	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$	
13,661		-331			21,700		
13,736	-335	13,638	${}^3A_{2g} \rightarrow {}^1E_g$	22,200			
13,996		-329					
14,065	-300						
14,296		-313					
14,378							
20,200		19,468	${}^3A_{2g} \rightarrow {}^1A_{1g}$				
22,600		22,065	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$				
27,200		28,800	${}^3A_{2g} \rightarrow {}^1T_{1g} + {}^1E_g$				
30,200							

^a $Dq = 770$, $F_2 = 1200$, $F_4 = 90$, $\lambda = 125$. ^b $Dq = 720$, $F_2 = 1200$, $F_4 = 90$, $\lambda = 125$.

 TABLE II
 OBSERVED ENERGIES (IN cm^{-1}) IN THE 5°K ABSORPTION SPECTRA OF NiBr_2 AND $\text{CdBr}_2\text{-Ni}^{2+}$

NiBr_2			$\text{CdBr}_2\text{-Ni}^{2+}$				
Obsd		Calcd ^a		Obsd	Calcd ^b	Assignment	
E	ΔE	E	Assignment	E	ΔE	E	
7,540		7,419	${}^3A_{2g} \rightarrow {}^3T_{2g}$	6,645		6,429	${}^3A_{2g} \rightarrow {}^3T_{2g}$
12,308				10,616		10,600	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$
12,370				11,416			
12,510	-202			11,820	-198		
12,568		-215		12,012		-183	11,963
12,700	-190	12,823	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$	12,195	-204		
12,765		-200	+				
12,890	190	11,500	$+ {}^1E_g$	12,399			
12,953		-188			16,800	16,962	${}^3A_{2g} \rightarrow {}^1T_{2g}$
13,158				18,116	19,117	${}^3A_{2g} \rightarrow {}^1A_{1g}$	
13,342				20,580	20,492	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$	
16,631							
16,681	-50	18,248	${}^3A_{2g} \rightarrow {}^1T_{2g}$				
19,841							
20,296							
20,492							
20,661	-169						
20,812	-151	20,289	${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$				
20,978	-166						
21,030	-152						
21,322							
21,459							
23,256							

^a $Dq = 740$, $F_2 = 1100$, $F_4 = 90$, $\lambda = 125$. ^b $Dq = 640$, $F_2 = 1100$, $F_4 = 85$, $\lambda = 150$.

13,324 and 13,405 cm^{-1} and the intense maximum which appears at 30,200 cm^{-1} . Figure 4 indicates that this latter band is first in evidence at 113°K. The double progression appears to be built on a $\sim 330\text{-cm}^{-1}$ vibrational mode with a separation between analogous members of $\sim 70\text{-cm}^{-1}$. Referring to Figure 3, we note that though a progression (now with a 290-cm^{-1} mode)

still exists in the spectrum of $\text{CdCl}_2\text{-Ni}^{2+}$ there is no longer a 70-cm^{-1} splitting present. In addition, the $30,200\text{-cm}^{-1}$ maximum is absent in the spectrum of $\text{CdCl}_2\text{-Ni}^{2+}$.

Some analogous features are observed in the spectrum of NiBr_2 , Figure 2. The broad prominent maxima decrease in intensity with decreasing temperature; how-

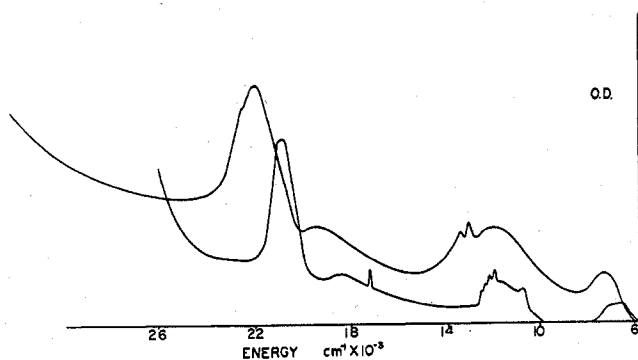


Figure 3.—The electronic spectra of $\text{CdCl}_2\text{-Ni}^{2+}$ (upper trace) and $\text{CdBr}_2\text{-Ni}^{2+}$ (lower trace).

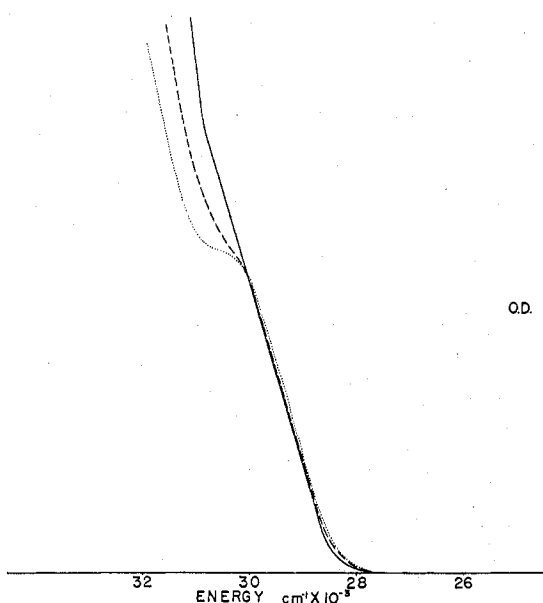


Figure 4.—The high band of NiCl_2 : —, 195°K; ---, 113°K; ···, 80°K.

TABLE III

VARIATION OF THE OSCILLATOR STRENGTH OF THE ${}^3A_{2g} \rightarrow {}^1X$ TRANSITION WITH TEMPERATURE AND CONCENTRATION

Compd	Transition	Temp, °K	$10^6 f$
NiCl_2	${}^3A_{2g} \rightarrow {}^1E_g$	80	0.58
		5	0.65
	${}^3A_{2g} \rightarrow {}^1A_{1g}$	300	5.67
		80	5.71
		5	5.84
		195	10.03 ^a
${}^3A_{2g} \rightarrow \text{exciton}$	113	10.65 ^a	
	80	10.12 ^a	
	5	10.15 ^a	
$\text{CdCl}_2\text{-Ni}^{2+}$	${}^3A_{2g} \rightarrow {}^1E_g$	5	0.66
		5	5.68
	${}^3A_{2g} \rightarrow \text{exciton}$	5	
NiBr_2	${}^3A_{2g} \rightarrow {}^1E_g$	5	0.54
		80	6.09
	${}^3A_{2g} \rightarrow {}^1A_{1g}$	5	8.74
$\text{CdBr}_2\text{-Ni}^{2+}$	${}^3A_{2g} \rightarrow {}^1E_g$	5	0.53
		5	5.53

^a Shoulder.

ever, the band at $19,841\text{ cm}^{-1}$ clearly increases in intensity below 80°K . The spectrum of NiBr_2 also shows a split vibrational progression in the $12,000\text{--}14,000\text{-cm}^{-1}$ region. Here the exciting frequency is on

the order of 200 cm^{-1} and the splitting $\sim 65\text{ cm}^{-1}$. This splitting is absent in $\text{CdBr}_2\text{-Ni}^{2+}$. A maximum analogous to the $30,200\text{-cm}^{-1}$ band, in NiCl_2 , is not observed due to the onset of an absorption edge at relatively low energies.

Discussion

For Ni(II) in an octahedral field the ground state is of 3A_2 symmetry. The spin-triplet excited states, in order of increasing energy, are 3T_2 , ${}^3T_1(\text{F})$, and ${}^3T_1(\text{P})$. Reduction of the symmetry to D_{3d} splits each of these excited states into an orbital singlet and an orbital doublet. There is no indication that this splitting is large enough to be detectable, however. (We shall see that the $\sim 70\text{-cm}^{-1}$ splitting of the sharper bands may be attributed to other causes.) The gross features of the spectra can therefore be assigned in octahedral symmetry. Using the calculations of Liehr and Ballhausen¹² we may assign the lowest energy bands in these halides to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition. This suggests a Dq of $\sim 770\text{ cm}^{-1}$ for NiCl_2 , $\sim 740\text{ cm}^{-1}$ for NiBr_2 , $\sim 730\text{ cm}^{-1}$ for $\text{CdCl}_2\text{-Ni}^{2+}$, and 660 cm^{-1} for $\text{CdBr}_2\text{-Ni}^{2+}$. The next broad maximum in each spectrum then clearly contains the ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ transition. This brings us to the progressions of relatively sharp maxima. Clearly, from their location and shape they most likely have as their origin a state which contains considerable 1E_g character. (Were they merely vibronic components of the ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ transition, they would commence at somewhat lower energies even when considering that the first members of the progressions are most likely pseudo-origins.) In addition the $\sim 70\text{-cm}^{-1}$ splitting which occurs in NiBr_2 and NiCl_2 must arise from a cooperative phenomenon or else it would be present in $\text{CdCl}_2\text{-Ni}^{2+}$ and $\text{CdBr}_2\text{-Ni}^{2+}$. We suggest that this splitting occurs due to exchange coupling in the magnetically concentrated compounds. This suggestion is further supported by the fact that the doublet at $16,631$ and $16,681\text{ cm}^{-1}$ in the spectrum of NiBr_2 , the ${}^3A_{2g} \rightarrow {}^1T_{2g}$ transition, remains split in $\text{CdBr}_2\text{-Ni}^{2+}$.

The next maximum, the ${}^3A_{2g} \rightarrow {}^1A_{1g}$ transition, which occurs at $20,000\text{ cm}^{-1}$ in NiCl_2 and NiBr_2 , exhibits a somewhat unusual behavior. (While it is true that this is not the normal assignment for the ${}^3A_{2g} \rightarrow {}^1A_{1g}$ transition, the presence of the sharp split band in both NiBr_2 and $\text{CdBr}_2\text{-Ni}^{2+}$ at $\sim 16,600\text{ cm}^{-1}$ appears to allow no alternative assignment. In addition there is precedent for such an assignment.¹³) In NiCl_2 there appears to be no significant change in intensity below 80°K even though other bands in the spectrum change markedly, while in NiBr_2 there is actually an increase in the intensity of this band below 80°K . This behavior is not repeated for Ni^{2+} in CdCl_2 and CdBr_2 . In addition the intensities of these maxima in relation to the next highest transition, ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$, are seen to decrease from the pure to the dilute Ni^{2+} -halide. This type of behavior is typical of a cooperative intensity mechanism³⁻⁵ which occurs only in the presence of spin waves. This appearance of this phenomena in NiCl_2 and NiBr_2 has also been noted by Kozielski, *et al.*,⁴ who attribute the breadth of the absorption band (magnon absorption bands are normally narrow) to

(13) B. D. Bird, G. A. Osborne, and P. J. Stephens, *Phys. Rev. B*, **5**, 1800 (1972).

electron-magnon coupling.¹⁴ Our experiments are consistent with this conclusion.

Turning our attention now to the maximum at 30,200 cm⁻¹ in the spectrum of NiCl₂ we note that it is completely absent in CdCl₂-Ni²⁺. On the surface this would tend to indicate an absorption process which is similar to that observed for the ³A_{2g} → ¹A_{1g} absorption band. Indeed Kozielski, *et al.*,⁴ have concluded that such is the case. Two phenomena dictate against this being either a short- or a long-range magnetic exchange process, however. The first is the total absence (in CdCl₂-Ni²⁺) of the transition even though the weaker (in NiCl₂) ¹T_{1g} and ¹A_{1g} bands are present. Since the concentration of Ni²⁺ is 10% in the CdBr₂-Ni²⁺ spectrum shown and 7% in the CdCl₂-Ni²⁺ spectrum, considerable numbers of pairs should be present. It follows then that a pairwise interaction would produce a band at 30,200 cm⁻¹. Second, the band is observed even at 113°K. This is some 63°K above the Neel temperature of NiCl₂ and would seem to be much too high a temperature for even moderate-range order to exist. This suggests that this maximum arises from the presence of a cooperative interaction of a type other than a magnetic one. Because of a lack of polarization it is not possible to determine the exact nature of the interaction.

(14) M. A. Krivoglatz and G. F. Levenson, *Sov. Phys.—Solid State*, **9**, 349 (1967).

CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO 87544

Structure of Tungsten Oxytetrafluoride¹

BY L. B. ASPREY, R. R. RYAN,* AND E. FUKUSHIMA

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Single-crystal X-ray intensity measurements on WOF₄ have been interpreted in terms of ordered tetrameric units with oxygen atoms assigned to the bridging positions.² The infrared spectrum of the solid showed a strong band at approximately 1050 cm⁻¹ which the authors interpreted in terms of a W-F stretching frequency due to an abnormally short W-F bond. It has been pointed out that this assignment is inconsistent with vibrational assignments in similar transition metal oxyfluoride compounds³ and alternate disordered structures containing fluorine bridges have been suggested for this material.⁴ Unfortunately the X-ray measurements are not sufficiently accurate to distinguish between the various proposed models.

We have made infrared and nmr measurements on the solid phase which lend convincing support to a model containing fluorine at the bridging positions in the tetramer.

Infrared Data.—Oxygen-18-substituted WOF₄ was

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

(2) A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 2074 (1968).

(3) I. R. Beattie and D. J. Reynolds, *Chem. Commun.*, 1531 (1968).

(4) M. J. Bennett, T. E. Haas, and J. F. Purdham, *Inorg. Chem.*, **11**, 207 (1972).

prepared by the reaction of WF₆ with H₂¹⁸O in the presence of HF and purified by sublimation. The composition of the material was established by single-crystal precession techniques. The infrared measurements were taken on a Perkin-Elmer 521 spectrometer from samples sublimed onto a CsCl window at liquid nitrogen temperature. The resulting spectrum shows the same structure in the region 500–750 cm⁻¹ as do the previously published spectra.² In addition a strong peak appears at 997 cm⁻¹ with a smaller peak at 1054 cm⁻¹. These peaks are, therefore, obviously due to W-¹⁸O and W-¹⁶O stretching frequencies, respectively.

Nuclear Magnetic Resonance.—A polycrystalline nmr sample was prepared by the same reaction and sealed in a polypropylene tube. At room temperature the ¹⁹F resonance is dominated by a motionally narrowed line with a width of 200 mG; this is an indication of molecular motion at a rate in excess of 10⁴ Hz. A spectrum without the narrowing is obtained at lower temperatures (–58 and –114°). The line recorded in the CW mode is 8 G wide and symmetric. Another line could be recorded only in the fast-passage mode because of extremely long spin-lattice relaxation time T₁ of between 3 and 4 min. In contrast, the first line has an estimated T₁ of 0.1 sec, three orders of magnitude shorter. From these observations we conclude that there are fluorine nuclei located in vastly different sites insofar as librational motion of WOF₄ is concerned; this is not consistent with a tetramer with all fluorines in terminal positions, no matter how chemically dissimilar those sites may be.

CONTRIBUTION NO. 4385 FROM THE ARTHUR AMOS NOYES LABORATORY OF CHEMICAL PHYSICS, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA 91109

Emission Lifetimes of Tungsten Carbonyl Complexes

BY MARK WRIGHTON,¹ GEORGE S. HAMMOND, AND HARRY B. GRAY*

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The behavior of excited states of coordination compounds has been investigated by studying photophysical processes, such as energy transfer^{2–5} and radiative decay⁶ as well as photochemistry.⁷ However, development of models for structure-reactivity relationships has been slow because of the lack of absolute rate data. For example, variations in quantum yields for a measurable process may be due either to an increase in the rate constant for that process or to a decrease in the rate constant for some competitive process. The

(1) National Institutes of Health Trainee.

(2) D. J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem.*, **72**, 3017 (1968).

(3) V. Balzani, R. Ballardini, M. T. Gondolfi, and L. Moggi, *J. Amer. Chem. Soc.*, **93**, 339 (1971).

(4) A. Pfeil, *ibid.*, **93**, 5393 (1971).

(5) J. N. Demas and A. W. Adamson, *ibid.*, **93**, 1800 (1971).

(6) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

(7) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, p 69.