

Notes

Contribution from the Department of Structural Studies,
Research Laboratory for Inorganic Chemistry,
Hungarian Academy of Sciences, Budapest H-1431, Hungary,
and Department of Chemistry and Institute of Materials
Science, University of Connecticut, Storrs, Connecticut 06268

Molecular Structure of Vanadium Dichloride and Chromium Dichloride from Electron Diffraction

Magdolna Hargittai,*^{1a} Olga V. Dorofeeva,²
and János Tremmel^{1b}

Received March 15, 1985

As a continuation of our research on the molecular structure of transition-metal dihalides, an electron diffraction investigation of vapor-phase vanadium dichloride and chromium dichloride has been carried out. Several first-row transition-metal dichlorides (MnCl_2 ,³ FeCl_2 ,⁴ and CoCl_2 ⁵) and dibromides (MnBr_2 ,⁶ FeBr_2 ,⁴ CoBr_2 ,⁷ and NiBr_2 ⁸) have already been investigated.

The single most interesting question of the geometry of these molecules is their shape. The linearity of the equilibrium structure of these molecules is well established despite recent controversy.^{9,10} Linearity has also been assumed^{11,12} for dihalides of other first-row transition metals. As interest toward these structures is mounting, we decided to probe such assumptions by an electron diffraction analysis of vanadium dichloride and chromium dichloride. Hereby experimental evidence is presented indicating the possibility of highly bent structures for these molecules.

Experimental Section

The samples of both VCl_2 and CrCl_2 were kindly provided by Professor Harald Schäfer, University of Münster.¹³ Both substances have low volatility; therefore, high-temperature experimental conditions had to be maintained during the electron-scattering experiments. Since the vapor composition of transition-metal dihalides may be complex, the combined electron diffraction/quadrupole mass spectrometric technique of the Budapest laboratory was utilized.¹⁴ The high-temperature nozzle¹⁵ was prepared from molybdenum. The nozzle temperatures were 1060 and 895 °C for VCl_2 and CrCl_2 , respectively. All other conditions of the electron-scattering experiments, data processing, and source of scattering factors were the same as in the other studies of the series.³⁻⁸ The molecular intensities and radial distributions are shown in Figures 1-4.

According to the mass spectra, the main components of the vapors in

- (1) (a) Visiting Scientist at the University of Connecticut (1983-1985), on leave from the Hungarian Academy of Sciences. (b) Hungarian Academy of Sciences.
- (2) Visiting Scientist at the Hungarian Academy of Sciences, Fall 1982, on leave from the Institute of High Temperatures, Soviet Academy of Sciences, Moscow, USSR.
- (3) Hargittai, I.; Tremmel, J.; Schultz, Gy. *J. Mol. Struct.* **1975**, *26*, 116.
- (4) Vajda, E.; Tremmel, J.; Hargittai, I. *J. Mol. Struct.* **1978**, *44*, 101.
- (5) Tremmel, J.; Ivanov, A. A.; Schultz, Gy.; Hargittai, I.; Cyvin, S. J.; Eriksson, A. *Chem. Phys. Lett.* **1973**, *23*, 533.
- (6) Hargittai, M.; Hargittai, I.; Tremmel, J. *Chem. Phys. Lett.* **1981**, *83*, 207.
- (7) Hargittai, M.; Dorofeeva, O. V.; Tremmel, J. *Inorg. Chem.* **1985**, *24*, 245.
- (8) Molnar, Zs.; Schultz, Gy.; Tremmel, J.; Hargittai, I. *Acta Chim. Acad. Sci. Hung.* **1975**, *86*, 223.
- (9) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *88*, 51.
- (10) Hargittai, M.; Hargittai, I. *J. Mol. Spectrosc.* **1984**, *108*, 155.
- (11) Hargittai, I.; Tremmel, J. *Coord. Chem. Rev.* **1976**, *18*, 257.
- (12) Hargittai, M. *Inorg. Chim. Acta* **1981**, L111.
- (13) Schäfer, H.; Laumanns, R. *Z. Anorg. Allg. Chem.* **1977**, *436*, 47.
- (14) Hargittai, I.; Bohatka, S.; Tremmel, J.; Berecz, I. *HSI, Hung. Sci. Instrum.* **1980**, *50*, 51. Schultz, Gy.; Tremmel, J.; Hargittai, I.; Berecz, I.; Bohatka, S.; Kagramanov, N. D.; Maltsev, A. K.; Nefedov, O. M. *J. Mol. Struct.* **1979**, *55*, 207.
- (15) Tremmel, J.; Hargittai, I. *J. Phys. E* **1985**, *18*, 148.

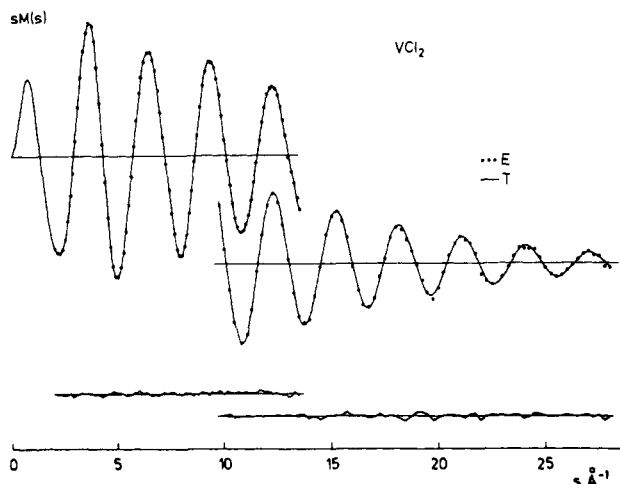


Figure 1. Experimental (E) and theoretical (T) molecular intensities for vanadium dichloride. The theoretical curve corresponds to model 1, Table I.

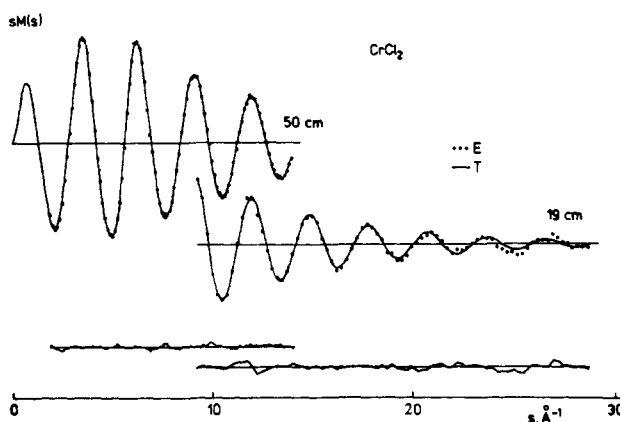


Figure 2. Experimental (E) and theoretical (T) molecular intensities for chromium dichloride. The theoretical curve corresponds to model 1, Table II.

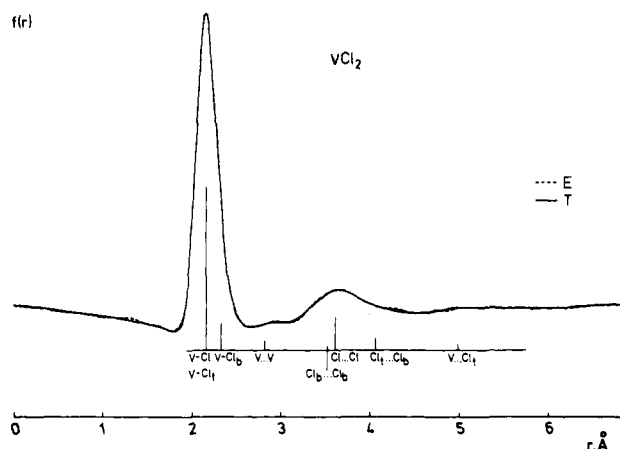


Figure 3. Radial distributions for vanadium dichloride corresponding to the molecular intensities of Figure 1.

both experiments were monomeric dichlorides. The presence of some 10% of dimeric species was indicated for vanadium dichloride. Considering the ion fragmentation mechanism, the presence of a small amount of vanadium tetrachloride could not be excluded. For chromium di-

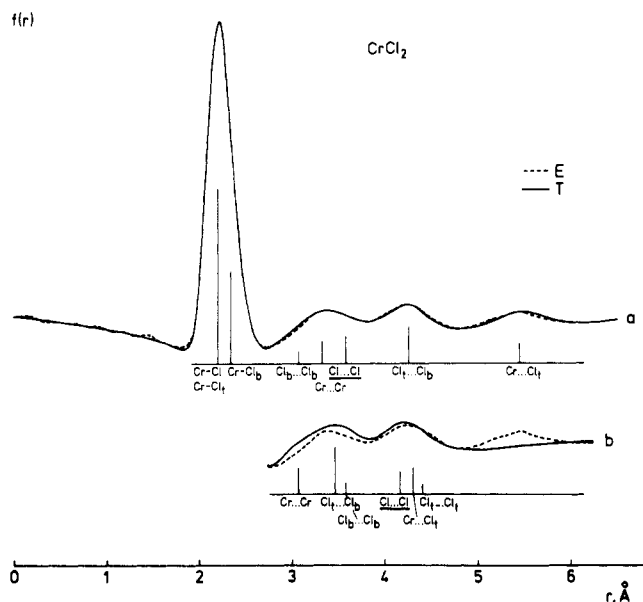
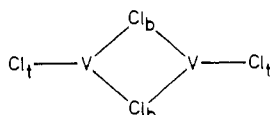


Figure 4. Radial distributions for chromium dichloride. (a) E and T correspond to curves E and T of Figure 2, respectively. (b) T corresponds to a model with a linear monomer. (The calculated monomer Cl...Cl contributions are underlined.)

chloride the mass spectra indicated a relatively large amount of dimeric species, about 20–25%.

Structure Analysis

Vanadium Dichloride. The two distinct peaks on the experimental radial distribution (Figure 3), to wit at about 2.16 and 3.65 Å, can be assigned to the V–Cl and Cl...Cl interactions, respectively. The corresponding bond angle Cl–V–Cl = 115° indicates a highly bent geometry. The agreement between the experimental and calculated distributions could be improved appreciably by including a small amount of dimeric species as suggested by the mass spectra. Subsequent refinements established a 9% presence of the dimeric species, in agreement with the mass spectrometric indications. In agreement with the findings for other substances,^{4,6,7} the model of the vanadium dichloride dimer was



The best dimer model possessed C_{2v} symmetry due to puckering of the four-membered ring, and the two terminal bonds were positioned equatorially. The ring puckering here may well be the consequence of low-frequency deformation vibrations, and the equilibrium ring conformation may be planar with coplanar terminal bonds (D_{2h} symmetry). Also, the two terminal bonds could be positioned axially, or one of them equatorially and the other axially. Such models have also been tested and could not be excluded although they showed somewhat worse agreement with the experimental data than the model with two equatorial terminal bonds.

The bridge V–Cl bonds were found to be considerably longer than the terminal bonds, while it was not possible to determine the difference between the length of the dimer terminal bonds and the bonds of the monomer. All this was consistent with our previous experience with similar systems.^{4,6,7} Table I presents two sets of results for vanadium dichloride. Set 1 originates from a refinement in which the monomer bond length and the terminal bond length of the dimer were assumed to be equal. Of course, the V–Cl distances in the monomer and dimer are most likely not the same. In order to examine the influence of such an assumption, set 2 was obtained when the terminal bond of the dimer was assumed to be 0.03 Å longer than the bond of the monomer. It is seen that even such a relatively drastic change in the assumption did not appreciably influence the other structural results.

As regards the presence of tetrachloride species, the possibility of a large relative abundance could be excluded by simple inspection of the experimental radial distribution. As the position of the second peak relative to the position of the principal peak corresponds to a near-tetrahedral angle, it is important to stress that the ratio of the areas under these maxima is very different from what would correspond to the VCl_4 structure. Whereas VCl_2 has two V–Cl interactions vs. one Cl...Cl interaction, VCl_4 has four V–Cl vs. six Cl...Cl. The possible presence of

Table I. Geometrical Parameters for VCl_2 (Estimated Total Errors in Parentheses)^a

	model 1 ^b	model 2 ^c
$r_g(V-Cl)_{\text{mean}},^d$ Å	2.172 (5)	2.173 (5)
Monomer		
$r_g(V-Cl),$ Å	2.172 (6)	2.170 (6)
$l(V-Cl),$ Å	0.080 (2)	0.080 (2)
$\kappa(V-Cl),$ Å ³	3.1×10^{-5} (6)	3.0×10^{-5} (6)
$r_g(Cl...Cl),$ Å	3.627 (15)	3.628 (15)
$l(Cl...Cl),$ Å	0.230 (12)	0.228 (12)
$\angle(Cl-V-Cl),$ deg	113.2 (8)	113.3 (7)
rel monomer amt, %	91 (2)	91 (2)
Dimer		
$r_g(V-Cl),$ Å	2.172	2.200
$l(V-Cl),^e$ Å	0.080	0.080
$r_g(V-Cl_b),$ Å	2.341 (16)	2.342 (15)
$l(V-Cl_b),^f$ Å	0.110	0.110
$\angle(Cl_b-V-Cl_b),$ deg	98.1 (13)	98.4 (12)
Calculated Mean Amplitudes of Vibration ^g		
	bent model (exptl geom)	linear model
$l(V-Cl),$ Å	0.089	0.091
$l(Cl...Cl),$ Å	0.241	0.120

^a For error estimation, see: Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *59*, 2513. In the error estimation of the distances and angles the influence of the assumptions in models 1 and 2 were taken into account. ^b Assumption: the monomer V–Cl distance and the dimer terminal V–Cl_t distance are assumed to be equal. ^c Assumption: $r(V-Cl)_{\text{monomer}} = r(V-Cl)_{\text{dimer}} - 0.03$ Å. ^d Mean of monomer V–Cl and dimer terminal V–Cl_t distances. ^e Assumed to be equal with $l(V-Cl)_{\text{monomer}}$. ^f The difference of the two bond amplitudes was constrained. ^g The experimental frequencies were taken from ref 17.

a smaller amount of tetrachloride species with an assumed geometry¹⁶ has been tested in the least-squares refinements. Including the tetrachloride species, however, worsened the agreement between experimental and theoretical distributions and led to unrealistic values of some parameters.

Matrix-isolation infrared spectra¹⁷ and electronic absorption spectra¹⁸ of vanadium dichloride have been interpreted in terms of linear geometry, and this structure has been rationalized.¹⁹ Accordingly, the present finding of a highly bent structure has to be scrutinized.

Attempts to interpret the experimental data by a linear dichloride structure, as the major component of the vapor, failed. In examining the possibility of a linear structure, we could rely on past experience with similar species, and the effects of large-amplitude bending vibrations were allowed for. Even linear equilibrium structures of transition-metal dihalides appear considerably bent (with a 160° rather than a 180° bond angle) in the electron diffraction analysis.¹⁰ In view of this effect, the Cl...Cl distance of linear VCl_2 would appear in the region 4.25–4.30 Å in the radial distribution curve. There is indeed a slight bump in the experimental radial distribution curve in this region, but it is far too small to account for a major contribution. If the monomer would be linear, then the major nonbonding contribution at 3.65 Å would have to be accounted for by other species. Both the dimer V_2Cl_4 and the tetrachloride VCl_4 have been tested in this respect. These attempts, however, did not give acceptable agreement between the experimental and theoretical distributions. Often there was no stable minimum in the refinement or the calculations led to unreasonable vibrational parameters.

Normal-coordinate analyses have been carried out for both vanadium dichloride and chromium dichloride, utilizing the experimental frequencies ν_2 and ν_3 from Hastie et al.¹⁷ The calculated vibrational amplitudes for both linear and bent models are collected in Tables I and II. These calculations suffered from the lack of ν_1 frequency, but the vibrational amplitudes are rather insensitive to reasonable changes in this frequency. As for the differences between the amplitudes calculated for the bent and linear geometries, the bond amplitudes are practically the same while the $l(Cl...Cl)$ values differ considerably. Comparisons with the experimental amplitudes yield good agreement for the bent model and marked disagreement for the linear one. On the other hand, the $l(Cl...Cl)$ value

(16) Morino, Y.; Uehara, H. *J. Chem. Phys.* **1966**, *45*, 4543.

(17) Hastie, J. W.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.* **1971**, *3*, 257.

(18) DeKock, C. W.; Gruen, D. M. *J. Chem. Phys.* **1966**, *44*, 4387.

(19) Drake, M. C.; Rosenblatt, G. M. *J. Electrochem. Soc.* **1979**, *126*, 1387.

Table II. Geometrical Parameters for CrCl₂ (Estimated Total Errors in Parentheses; Footnotes As in Table I)

	model 1 ^b	model 2 ^c
$r_g(\text{Cr}-\text{Cl})_{\text{mean}},^d \text{ \AA}$	2.207 (7)	2.208 (8)
Monomer		
$r_g(\text{Cr}-\text{Cl}), \text{ \AA}$	2.207 (10)	2.200 (11)
$l(\text{Cr}-\text{Cl}), \text{ \AA}$	0.090 (3)	0.089 (3)
$\kappa(\text{Cr}-\text{Cl}), \text{ \AA}^3$	4.5×10^{-5} (18)	4.3×10^{-5} (16)
$r_g(\text{Cl}\cdots\text{Cl}), \text{ \AA}$	3.612 (44)	3.644 (44)
$l(\text{Cl}\cdots\text{Cl}), \text{ \AA}$	0.256 (48)	0.266 (50)
$\angle(\text{Cl}-\text{Cr}-\text{Cl}), \text{ deg}$	109.8 (24)	111.8 (25)
rel monomer amt, %	72 (5)	73 (5)
Dimer		
$r_g(\text{Cr}-\text{Cl}_2), \text{ \AA}$	2.207	2.230
$l(\text{Cr}-\text{Cl}_2),^e \text{ \AA}$	0.090	0.089
$r_g(\text{Cr}-\text{Cl}_2), \text{ \AA}$	2.353 (10)	2.357 (10)
$l(\text{Cr}-\text{Cl}_2),^f \text{ \AA}$	0.120	0.119
$\angle(\text{Cl}_2-\text{Cr}-\text{Cl}_2), \text{ deg}$	82.0 (7)	82.8 (8)
Calculated Mean Amplitudes of Vibration ^g		
	bent model (exptl geom)	linear model
$l(\text{Cr}-\text{Cl}), \text{ \AA}$	0.087	0.090
$l(\text{Cl}\cdots\text{Cl}), \text{ \AA}$	0.280	0.121

calculated for the linear geometry coincides with the one determined experimentally for linear FeCl₂, 0.119 Å.¹⁰

Chromium Dichloride. The experimental radial distribution (Figure 4) as well as the mass spectra indicated a large relative abundance of the dimeric species. The refinement eventually showed a 30% presence for the dimeric species. Considering the larger relative weight of the dimer vs. the monomer as regards scattering power, this situation considerably hindered the determination of an accurate structure for CrCl₂. On the other hand, our early hope for a more detailed elucidation of the dimer geometry did not prove feasible because of the strong correlation among the parameters. The refinements again yielded a highly bent geometry for the monomer; the results are compiled in two parameter sets in Table II, similarly to those for vanadium dichloride.

It has been tested thoroughly whether or not the experimental data could be approximated by a model in which the monomer was linear. In fact, an earlier electron diffraction report on chromium dichloride²⁰ communicated 2.20 (1) and 4.34 (5) Å for the Cr-Cl bonded and Cl...Cl nonbonded distances which in turn yield a 161° bond angle. This, taking into account the probable shrinkage,¹¹ would correspond to a linear equilibrium geometry. There is, in fact, a peak at 4.25 Å on our radial distribution curve (Figure 4), which could correspond to the Cl...Cl interaction of a linear monomeric CrCl₂ molecule. Assuming the Cl...Cl distance to appear in this peak and constraining it at various values, we refined its amplitude to very large values (0.37 Å), which is unrealistic for a linear molecule according to our earlier experience¹⁰ and to the calculated values given in Table II. In this model the geometry of the dimer had to be taken such that its main nonbonded contribution, the Cl...Cl distance, shifts from the 4.25-Å peak to the 3.4-Å one (see curve b in Figure 4, where the corresponding part of the radial distribution curve of this model, together with the experimental curve, is indicated). This could only be achieved with unrealistically tilted terminal bonds for the dimer. In this model the Cr...Cl, nonbonded distance of the dimer shifts from the 5.4-Å peak to the 4.25-Å one, causing marked disagreement between the experimental and theoretical distributions. Moreover, when the Cl...Cl distance of the monomer was allowed to vary, it shifted to the maximum at 5.4 Å, rendering the model meaningless.

Discussion

Our high-temperature gas-phase electron diffraction data are consistent with highly bent shapes of the vanadium dichloride and chromium dichloride molecules. This result represents a challenge to the spectroscopist to determine the ν_1 symmetric stretching frequency in the infrared spectrum. It also represents a challenge to the theoretical chemist to account for the structural differences among the dichlorides of first-row transition metals. Quantum-chemical calculations on manganese dichloride²¹ suggest that there are two orbitals with substantial d character that markedly change their energy on bending; they are the σ (d_{z^2}) and one of the π (d_{yz}) orbitals of the linear molecule. The energy of the first decreases

and that of the second increases upon bending. Thus, the bent geometry of VCl₂ and CrCl₂ could be rationalized with an electronic configuration in which the d_{yz} orbital would be empty and the d_{z^2} orbital half-filled, and the molecules would favor a bent geometry with a lower total energy than for the linear configuration. Unfortunately, these systems are not easily amenable to sophisticated calculations, which is especially demonstrated by the uncertainties in the determination of the bond lengths.²¹ Reliable information even merely on the bond length differences could facilitate a better utilization of the available experimental data. A more accurate determination of the bond lengths of these dihalides from the experiment is hindered by the lack of knowledge of the difference between the lengths of the monomer bond and the terminal bond of the dimer. Further vibrational spectroscopic information would also enhance the utility of our electron diffraction data.

Acknowledgment. We express our gratitude to Professor Harald Schäfer, University of Münster, for the samples of vanadium dichloride and chromium dichloride. We appreciate the advice and encouragement from Prof. L. V. Gurvich and Prof. I. Hargittai and some auxiliary computations by Dr. B. Rozsondai.

Registry No. VCl₂, 10580-52-6; CrCl₂, 10049-05-5.

Supplementary Material Available: Listings of total electron diffraction intensities for two camera distances (50 and 19 cm) for both compounds (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and
Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Replacement of Acetate Ions in Dimolybdenum Tetraacetate by Acetonitrile Molecules: Crystal Structures of Two Compounds Containing the *cis*-[Mo₂(O₂CCH₃)₂(CH₃CN)₄]²⁺ Cation

F. Albert Cotton,* Austin H. Reid, Jr., and Willi Schwotzer

Received August 6, 1984

Over a number of years the reactions of dimolybdenum(II) carboxylates, especially the acetate, Mo₂(O₂CCH₃)₄, with strong acids have provided synthetic routes to many other compounds having the Mo₂⁴⁺ binuclear cation at the center.¹ Doubtless the most important of such reactions is the one² used to obtain the [Mo₂Cl₄]⁴⁺ ion, from which scores of other Mo₂⁴⁺ compounds are then prepared.

There have also been several efforts, with varying degrees of success, to replace carboxylate groups with weakly coordinating anions (e.g., CF₃SO₃⁻) or with neutral ligands so as to obtain highly reactive complexes that might be of use synthetically. Bowen and Taube³ were able to obtain the Mo₂⁴⁺(aq) ion and to form the [Mo₂(en)₄]⁴⁺ complex, but neither of these cationic species has been obtained in a crystalline compound suitable for X-ray crystallographic characterization. Abbott and co-workers have studied reactions of Mo₂(O₂CCH₃)₄ with CF₃SO₃H⁴ and later of Mo₂(O₂CH)₄ with CF₃SO₃H.⁵ The former yielded,

- (1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
- (2) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7, 2698; **1970**, *9*, 346.
- (3) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287; *Inorg. Chem.* **1974**, *13*, 2245.
- (4) Abbott, E. H.; Schoenewolf, F., Jr.; Backstrom, T. *J. Coord. Chem.* **1974**, *3*, 255.
- (5) Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774.

(20) Kupreev, A. V., unpublished results.

(21) Hargittai, M.; Rossi, A. *Inorg. Chem.*, in press.