

We have been able to prepare Zn(gma) as blue and red forms. The blue form is soluble in DMF but a red form soon precipitates and is probably polymeric, or at least dimeric material. The single isotropic resonance in glasses of reduced blue material (which we attribute to the monomer) invariably is accompanied by satellites attributable to zero-field splitting in a molecular triplet state. A half-field $\Delta M_S = 2$ transition is also observed. These observations are consistent with our suggestion of polymerization in these systems.

We have shown that in the complex Ni(gma)⁻, the deviation of the principal g values from that of a free spin is a result of the participation of metal orbitals in the molecular orbital of the odd spin. The isotropic g values of Zn(gma)⁻ and Cd(gma)⁻, which are both properly described as containing radical ligands, are almost identical with that of a free electron. This result demonstrates that spin-orbit coupling due to ligand atoms does not lead to large g shifts in these complexes. The larger g shifts for Ni(mnt)₂⁻ and Ni(tdt)₂⁻ suggest that the metal orbital participation in the half-filled molecular orbital is larger than in Ni(gma)⁻. Therefore, the description⁵ of all three anions as Ni(II)-radical-ligand complexes is oversimplified, and the basis on which it was proposed (*i.e.*, the supposed similarity of the g tensors of the three Ni anions) is vitiated by the present investigation. We suggest that g tensors which are isotropic and close to that of a free electron are diagnostic evidence for cation-stabilized radicals in these and similar thio ligand systems. It is clear that what is needed is a theory which will allow the quantitative interpretation of spin-Hamiltonian parameters for systems where there is extensive delocalization of the unpaired electrons over the ligands. This is a formidable theoretical problem, but its solution would help to cast further light on the electronic structures of many interesting paramagnetic chelates.

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—1) of the diamagnetic six-coordinate complexes MoS₆C₆(CF₃)₆ⁿ and WS₆C₆(CF₃)₆ⁿ, the electron is removed from a ligand-localized orbital. We found that the oxidation half-wave potentials were +0.36 to +0.32 v, respectively, further supporting our argument that the particular metal atom has little effect (except by its charge) on the oxidation-reduction potential when a ligand electron is involved.

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(18) (a) Alfred P. Sloan Foundation Fellow; (b) NSF Predoctoral Fellow, 1963–1966.

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Structural Characterization of a New Niobium Subhalide, Nb₆I₁₁, Containing the First Known [M₆X₃]ⁿ Group with Nonintegral Metal Oxidation State

Sir:

Considerable experimental and theoretical work^{1–17} recently has been directed toward the characterization

(1) P. W. Seabaugh and J. D. Corbett, *Inorg. Chem.*, **4**, 176 (1965), and references cited therein.

of niobium and tantalum subhalides, in which for several phases the structures have a common hexanuclear metal building block of stoichiometry [M₆X₁₂]ⁿ (with $n = +2$, $+3$, and $+5(?)$ reported in the solid state and $n = +2$ and $+4$ in solution). These hexameric ions of niobium and tantalum, containing an octahedral metal framework with halogen atoms bridging the edges, exhibit unusually rich electronic spectra characteristic of polynuclear metal complexes with strong metal-metal interactions.

We wish to report the structural determination of a new polynuclear niobium metal cluster Nb₆I₁₁, which as the lowest found niobium subhalide contains the first [M₆X₃]ⁿ species observed for the group V transition elements. The identity of Nb₆I₁₁ was established by an X-ray investigation of a single crystal from a sample of Nb₃I₈,¹ generously furnished to us by Professor J. D. Corbett and Dr. M. A. Kust of Iowa State University (Ames), which had been partially disproportionated during a transpiration study of vaporization. The phase NbI_{1.83} (or Nb₆I₁₁) first was isolated by Schäfer and Simon^{7,14} who proposed as most probable the correct structural formula [Nb₆I₈]³⁺(I⁻)₃.

The compound crystallizes in an orthorhombic unit cell with symmetry Pccn (D_{2h}¹⁰) and lattice parameters $a = 15.31 \pm 0.03$, $b = 11.34 \pm 0.03$, and $c = 13.58 \pm 0.03$ Å. Considerable difficulty was encountered in obtaining a suitable single crystal for X-ray measurements owing to moisture sensitivity and crystal twinning problems. The subsequent structural determination revealed four formula species of Nb₆I₁₁ per unit cell with $\rho_{\text{calcd}} = 5.21$ g cm⁻³. After unsuccessful attempts to interpret Patterson and superposition maps for the presumed Nb₃I₈, both the configuration and correct composition were elucidated by the application of a symbolic addition method of phase determination.¹⁸ The present anisotropic least-squares refinement gives $R_1 = 9.8\%$ and $R_2 = 10.2\%$ for the 1087 observed, independent reflections collected photographically with Mo K α radiation.

The structure consists of [Nb₆I₈]³⁺ groups with a configuration (Figure 1) in which the six niobium atoms are arranged octahedrally about a crystallographic center of symmetry with the eight iodine atoms symmetrically located above the triangular faces.

(2) H. Schäfer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964), and references cited therein.

(3) L. D. Crossman, D. P. Olsen, and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).

(4) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(5) M. B. Robin and N. A. Kuebler, *ibid.*, **4**, 978 (1965).

(6) R. J. Allen and J. C. Sheldon, *Australian J. Chem.*, **18**, 277 (1965).

(7) A. Simon, H. G. Schnering, H. Wöhrle, and H. Schäfer, *Z. Anorg. Allgem. Chem.*, **339**, 155 (1965).

(8) P. F. Gortsema and R. Didchenko, *Inorg. Chem.*, **4**, 182 (1965).

(9) H. Schäfer, H. G. Schnering, K.-J. Niehues, and H. G. Nieder-Vahrenholz, *J. Less-Common Metals*, **9**, 95 (1965).

(10) R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, **2**, 547 (1963).

(11) H. Schäfer, H. Scholz, and R. Gerken, *Z. Anorg. Allgem. Chem.*, **331**, 154 (1964).

(12) H. Schäfer, D. Bauer, W. Beckmann, R. Gerken, H. G. Nieder-Vahrenholz, K.-J. Niehues, and H. Scholz, *Naturwissenschaften*, **51**, 241 (1964).

(13) H. Schäfer, R. Gerken, and H. Scholz, *Z. Anorg. Allgem. Chem.*, **335**, 96 (1965).

(14) D. Bauer, H. G. Schnering, and H. Schäfer, *J. Less-Common Metals*, **8**, 388 (1965).

(15) P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965).

(16) R. E. McCarley and J. C. Boatman, *ibid.*, **4**, 1486 (1965).

(17) R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *ibid.*, **4**, 1491 (1965).

(18) Cf. I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

The cluster alternatively may be described as a cube of iodine atoms with the niobium atoms centered on each face. This cube is circumscribed by an octahedron of six iodine atoms which extend radially outward from the apices of the niobium cluster. Each of these latter iodine atoms symmetrically bridges two $[\text{Nb}_6\text{I}_8]^{3+}$ groups such that the formula may be written as $[\text{Nb}_6\text{I}_8]^{3+}(\text{I}^-)_{6/2}$. To date this general $[\text{M}_6\text{X}_8]^n$ configuration has only been shown for several complexes containing the $[\text{Mo}_6\text{X}_8]^{4+}$ and $[\text{W}_6\text{X}_8]^{4+}$ ions.^{2, 19, 20}

In contrast to these molybdenum and tungsten analogs which possess a formal oxidation state of +2 and a closed-shell electronic configuration, the $[\text{Nb}_6\text{I}_8]^{3+}$ ion has a nonintegral niobium oxidation state and an open-shell electronic configuration. Each niobium atom in Nb_6I_{11} has an average formal oxidation state of $+11/6$ (or +1.83); the crystallographically required C_i molecular symmetry (by which the six niobium atoms are related in pairs to each other) precludes the assignment of integral oxidation states (e.g., one +1 and five +2) to the niobium atoms. Although the experimentally observed number of unpaired electrons as yet is unknown for Nb_6I_{11} , the formula requires at least a doublet ground state corresponding to one unpaired electron which no doubt is delocalized over the entire $[\text{Nb}_6\text{I}_8]^{3+}$ group.

The $[\text{Mo}_6\text{Cl}_8]^{4+}$ ion was determined from X-ray analyses by Brosset¹⁹ to have (within rather large uncertainties of at least 0.05 Å) an approximate cubic configuration of O_h symmetry. A salient structural feature of the $[\text{Nb}_6\text{I}_8]^{3+}$ ion, however, is its pronounced distortion from a regular octahedral geometry to one of only centrosymmetry, C_i . The observed over-all environment of the Nb_6 fragment can be considered to arise from a shift of the apical niobium atoms, $\text{Nb}(1)$ and $\text{Nb}(1')$, such that the $\text{Nb}(1)\text{--Nb}(1')$ line is inclined from the normal of the basal plane of four niobium atoms (*viz.*, $\text{Nb}(2)$, $\text{Nb}(2')$, $\text{Nb}(3)$, and $\text{Nb}(3')$) by approximately 2° toward $\text{Nb}(2')$ and by 5° toward $\text{Nb}(3')$. This deviation is reflected in the following Nb–Nb distances: $\text{Nb}(1)\text{--Nb}(2)$, 2.88 Å; $\text{Nb}(1)\text{--Nb}(2')$, 2.80 Å; $\text{Nb}(1)\text{--Nb}(3)$, 2.94 Å; $\text{Nb}(1)\text{--Nb}(3')$, 2.72 Å; $\text{Nb}(2)\text{--Nb}(3)$, 2.88 Å; and $\text{Nb}(2')\text{--Nb}(3)$, 2.88 Å. The *trans* $\text{Nb}(1)\text{--Nb}(1')$ distance of 3.96 Å also is 0.1 Å shorter than the average value of 4.07 Å for the other two equivalent *trans* Nb–Nb distances (4.06 and 4.08 Å) for the four basal niobium atoms. The average *cis* Nb–Nb distance of 2.85 Å compares favorably both with the shortest Nb–Nb distance in niobium metal (2.86 Å)²¹ and with the average *cis* Nb–Nb distance for the $[\text{Nb}_6\text{X}_{12}]^n$ group in solution as $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ (2.85 Å with assumed O_h symmetry)²² and in the solid state as $[\text{Nb}_6\text{Cl}_{12}]^{2+}(\text{Cl}^-)_2$ (2.925 Å with tetragonal D_{4h} symmetry)⁷ and $[\text{Nb}_6\text{F}_{12}]^{3+}(\text{F}^-)_3$ (2.80 Å with cubic O_h symmetry).⁹ Longer Nb–Nb distances are found in $\alpha\text{-NbI}_4$ (3.31 Å)²³ and NbOI_2 (3.16 Å),² both of which possess Nb_2 interactions involving the pairing of electrons.

(19) C. Brosset, *Arkiv Kemi, Mineral. Geol.*, **20A**, No. 7 (1945); **22A**, No. 11 (1946); C. Brosset, *Arkiv Kemi*, **1**, 353 (1950); P. A. Vaughan, *Proc. Natl. Acad. Sci. U. S.*, **36**, 461 (1950).

(20) J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960).

(21) Cf. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p. S7.

(22) P. A. Vaughan, J. H. Sturdivant, and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950).

(23) L. F. Dahl and D. L. Wampler, *Acta Cryst.*, **15**, 903 (1962).

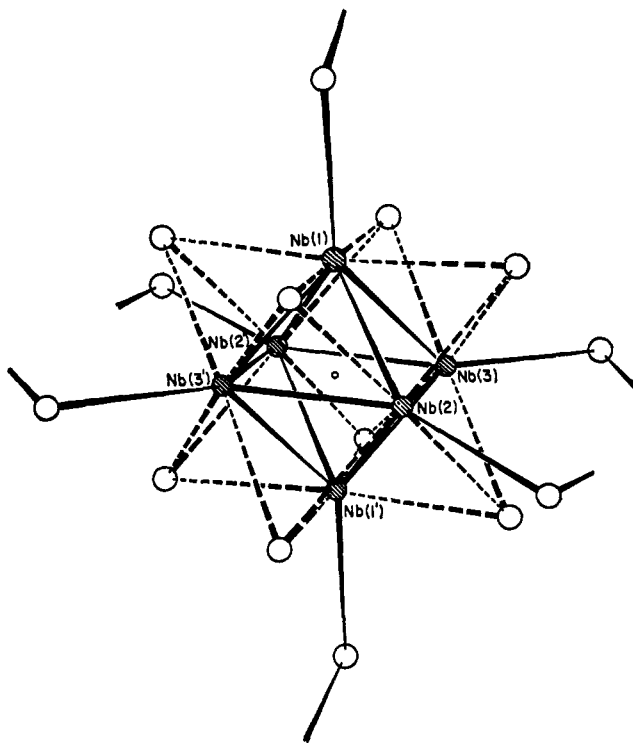


Figure 1. The molecular configuration of the $[\text{Nb}_6\text{I}_8]^{3+}(\text{I}^-)_{6/2}$ group.

The small but significant deviations of the triply bridged iodine atoms of the $[\text{Nb}_6\text{I}_8]^{3+}$ ion from the corners of a cube can be readily explained from the niobium positions. The $\text{I}\cdots\text{I}$ contacts for the face of the iodine cube containing the apical $\text{Nb}(1)$ are 4.06, 4.24, 4.04, and 3.88 Å, where the shift of $\text{Nb}(1)$ is in the direction of the elongated side. The doubly bridged iodine attached to $\text{Nb}(1)$ also follows the directional shift of $\text{Nb}(1)$ in that the $\text{I}(\text{doubly bridged})\cdots\text{I}(\text{triply bridged})$ contacts toward which $\text{Nb}(1)$ and the doubly bridged iodine have shifted are closer together than those away from which $\text{Nb}(1)$ and the doubly bridged iodine have shifted (3.93 Å *vs.* 4.17 Å). However, the twelve crystallographically independent distances from the niobium atoms to the triply bridged iodines of the $[\text{Nb}_6\text{I}_8]^{3+}$ group remain almost invariant under this distortion, ranging from 2.84 to 2.90 Å with an average value of 2.87 Å; the mean of the Nb–I(doubly bridged) distances (2.90, 2.96, and 2.93 Å) is 2.93 Å. Individual estimated standard deviations of 0.01 Å for all bond lengths were obtained from a full-matrix least-squares refinement.²⁴

With the assumption that the molecular orbital energy level diagram calculated by Cotton and Haas⁴ for $[\text{Mo}_6\text{Cl}_8]^{4+}$ is also qualitatively applicable for $[\text{Nb}_6\text{I}_8]^{3+}$, the 19 valence electrons for the Nb_6 framework occupy all the metal–metal bonding orbitals $d_{22}(a_{1g})$, $d_{zz}d_{yz}(t_{1u})$, $d_{zz}d_{yz}(t_{1g})$, and $d_{x^2-y^2}(e_g)$ with one

(24) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962; W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

unpaired electron in the $d_{x^2-y^2}(t_{2u})$ MO.²⁵ Based on this bonding representation the over-all ground-state electronic configuration is T_{2u} . In order to attribute at least partly this crystallographic distortion of the $[\text{Nb}_6\text{I}_8]^{3+}$ ion from regular octahedral O_h symmetry to a *Jahn-Teller phenomena* (as differentiated from anisotropic coulombic forces), it is only necessary that the ground electronic state be degenerate. Such a situation would result either when one unpaired electron occupies a degenerate orbital (provided the other electrons are all spin paired) or when three spin-free electrons occupy a doubly degenerate orbital.

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(25) The Cotton-Haas molecular orbital metal atom cluster model applied to $[\text{Mo}_6\text{X}_8]^{4+}$ and $[\text{M}_6\text{Cl}_{12}]^{2+}$ ($\text{M} = \text{Nb}, \text{Ta}$) presumes an ordering of one-electron energy levels based on molecular orbital calculations involving only metal-metal interactions (with the perfect pairing approximation allowing separability with regard to metal-halogen interactions).⁴ It should be noted that another molecular orbital calculation involving both metal-metal and metal-halogen interactions was applied to $[\text{M}_6\text{X}_{12}]^{2+}$ ($\text{M} = \text{Nb}, \text{Ta}$) by Robin and Kuebler,⁵ and their resulting energy level pattern was considerably different from the Cotton-Haas energy level scheme for $[\text{Nb}_6\text{Cl}_{12}]^{2+}$. No doubt more rigorous MO treatments of these metal cluster systems will be necessary in order to clarify the orbital ordering for even the ground-state configuration (apart from the far more difficult problem of rationalizing the electronic spectra).

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The Aggregation of Acridine Orange in Aqueous Solution¹

Sir:

The optical properties of dye molecules in aqueous solution have been studied extensively for a number of years.² Of particular interest have been the changes

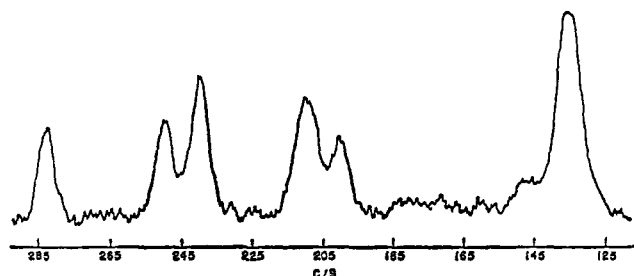
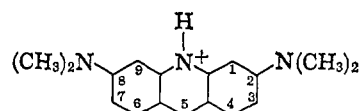


Figure 1. Nmr spectrum of the ring protons for acridine orange cation in D_2O (120 scans); 0.02 M .

(1) This work was supported by the U. S. Atomic Energy Commission.

(2) (a) S. E. Sheppard, *Proc. Roy. Soc. (London)*, **A28**, 256 (1909); (b) V. Zanker, *Z. Physik. Chem.*, **199**, 225 (1952); (c) *ibid.*, **200**, 250 (1952); (d) G. R. Haugen and W. H. Melhuish, *Trans. Faraday Soc.*, **60**, 386 (1964); (e) M. K. Pal and M. Schubert, *J. Phys. Chem.*, **67**, 1821 (1963); (f) M. E. Lamm and D. M. Neville Jr., *ibid.*, **69**, 3872 (1965).

observed in the visible region of the spectrum³ for anionic dyes with a planar ring structure as the dye concentration is increased.^{2b,e} These changes are generally interpreted in terms of an aggregation of the dye molecules to form dimers, trimers, and larger polymeric species at higher concentration.^{1b,c,f} Although the structure of the aggregate cannot be established from the optical spectrum, the hypochromism and shift of λ_{max} can be interpreted theoretically by exciton theory⁴ in terms of a parallel stacking of the adjacent rings in the aggregate (as opposed to a coplanar orientation of adjacent rings). In principle, it should be possible to confirm the most favored orientation of rings in the aggregate experimentally by following the proton chemical shifts as a function of dye concentration. If the rings are stacked parallel to each other, then a shift to low field would be noted for the ring protons upon dilution (disaggregation); if the rings are initially aggregated in a coplanar configuration, then dilution would produce a high-field shift. In this communication we wish to report the results of a study of the concentration dependence of the proton chemical shifts for the cationic dye, acridine orange (AO), in D_2O .



Dilute solutions of highly purified⁵ AO cation were made up in 90% D_2O –10% H_2O , and the spectra were recorded with a Varian DA-60 spectrometer at room temperature ($25 \pm 1^\circ$). Because of the low concentrations (10^{-2} – 10^{-4} M) of AO a Varian C-1024 time-averaging computer was used to enhance the signal-to-noise ratio. Figure 1 shows the spectrum obtained for the ring protons of a 10^{-2} M AO solution after 120 scans. The spectra were calibrated by superimposing audio side bands of the water signal on the spectrum in the final scan.

The analysis of the AO spectra is straightforward and a summary of the chemical shifts and coupling constants is given in Table I. The errors for these param-

Table I

Concn, M	No. of scans	δ_{CH_3} ^{a,b}	δ_5	$\delta_{1(9)}$	$\delta_{3(4)}$ ^c	$J_{3(4)(7)}$ ^d , cps
1.0×10^{-2}	120	21.9	−282.2	−134.1	−224.9	9.7
5.0×10^{-4}	6700	3.5	−312.8	−178.7	−251.3	9.3

^a ± 2.0 cps. ^b δ values are relative to a trace of $(\text{CH}_3)_4\text{NBr}$ as internal reference. ^c Midpoint of AB spectrum. ^d ± 0.5 cps.

eters are somewhat larger than normal and reflect an uncertainty in line positions due to the relatively large

(3) Hypochromism and shift of λ_{max} to shorter wavelength.

(4) (a) H. Devoe, *J. Chem. Phys.*, **41**, 393 (1964); (b) M. Kasha, *Radiation Res.*, **20**, 55 (1963).

(5) Kindly supplied by Dr. L. Bunville of Argonne National Laboratory.