

Figure 2. Representation of the structures for the $\text{Mo}_6\text{I}_8^{4+}$ and $\text{Mo}_4\text{I}_7^{2+}$ cluster cores showing the close relation between the two units.

able. However, we may surmise that loss of one I atom from the I_8 cube is necessary to permit close approach and bonding between Mo(1) and Mo(2). In $\text{Mo}_6\text{X}_8^{4+}$ clusters the distance between trans Mo atoms is ca. $\sqrt{2}(2.60) = 3.67 \text{ \AA}$.⁷ With all eight I atoms retained in the cube, this distance cannot contract without large translation of the trans Mo atoms toward the interior of the cube, i.e., out of the plane of the surrounding I atoms. Thus, better Mo-Mo bonding resulting from this translation would be opposed by unfavorable electrostatic interactions. Loss of one I atom from the I_8 cube overcomes the latter problem and permits much stronger bonding between Mo(1)-Mo(2).

Thus $\text{Mo}_4\text{I}_7^{2-}$ becomes the second example of a cluster which is best viewed as a fragment of the $\text{Mo}_6\text{X}_8^{4+}$ unit; the ion $\text{Mo}_5\text{Cl}_{13}^{2-}$ represents the first.⁸ In the latter case formation of the $\text{Mo}_5\text{Cl}_8^{3+}$ core formally requires only removal of one Mo^+ atom from the $\text{Mo}_6\text{Cl}_8^{4+}$ unit. The Mo-Mo distances of 2.602 (3) and 2.563 (3) \AA reported for $\text{Mo}_5\text{Cl}_{13}^{2-}$ are quite comparable with the distances for the five short bonds of $\text{Mo}_4\text{I}_7^{2-}$. By comparison with $\text{Mo}_6\text{X}_8^{4+}$ clusters the ready removal of one electron per cluster, as dictated for the net oxidation states of 2.20 and 2.25 per Mo for $\text{Mo}_5\text{Cl}_{13}^{2-}$ and $\text{Mo}_4\text{I}_7^{2-}$, respectively, appears to be a result of abundant nonbonding electrons localized on the basal Mo atoms of $\text{Mo}_5\text{Cl}_{13}^{2-}$ and on Mo(1) and Mo(2) of $\text{Mo}_4\text{I}_7^{2-}$. These in turn may be ascribed to the "unsatisfied" orbitals created by the removal of either one or two metal atoms from the $\text{Mo}_6\text{X}_8^{4+}$ unit.^{9,10}

The structure of $\text{Mo}_4\text{I}_7^{2-}$ also may be compared with those of $\text{CsNb}_4\text{X}_{11}$ ($\text{X} = \text{Cl}$ or Br)¹¹ and $\text{Mo}_4\text{S}_4\text{Br}_4$.¹² In each of the latter cases the formal M-M bond order may be assigned a value of 1.0. Yet in both cases the average M-M bond distances are much longer than in $\text{Mo}_4\text{I}_7^{2-}$, viz., 2.86 \AA for $\text{CsNb}_4\text{Cl}_{11}$, 2.98 \AA for $\text{CsNb}_4\text{Br}_{11}$, and 2.80 \AA for $\text{Mo}_4\text{S}_4\text{Br}_4$. Neither of the $\text{CsNb}_4\text{X}_{11}$ or $\text{Mo}_4\text{S}_4\text{Br}_4$ structures is capable of housing all 15 of the metal electrons found in $\text{Mo}_4\text{I}_7^{2-}$ without occupation of antibonding orbitals.^{13,14} A rough MO analysis of the Mo-Mo bonding in $\text{Mo}_4\text{I}_7^{2-}$ indicates that there are six bonding and two nonbonding orbitals available to accommodate the 15 electrons.¹⁰ The formal Mo-Mo bond order is thus 1.0 (12 electrons, six bonds) and 3 electrons reside in nonbonding orbitals localized mainly on Mo(1) and Mo(2). Since in C_{2v} symmetry these orbitals are nondegenerate, the cluster ion should have a magnetic moment corresponding to one unpaired electron. The observed moment $\mu = 1.87 \mu_B$ is temperature independent and in agreement with this requirement.

The presence of the formally nonbonding MO's with 3 electrons indicates that $\text{Mo}_4\text{I}_7^{2-}$ should exhibit interesting redox chemistry. Also the electron-rich character of this cluster suggests that it should be unusually susceptible to attack by electrophilic reagents and addition of metal atoms to expand the cluster. These aspects of the chemistry are presently under investigation.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

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- (4) Somewhat higher yields can be obtained, $\sim 90\%$, by a variant of the procedure whereby both $\text{Mo}(\text{CO})_6$ and I_2 are added in accordance with the equation $3\text{Mo}(\text{CO})_6 + \text{Mo}(\text{CO})_6 + \frac{3}{2}\text{I}_2 = \text{Mo}_4\text{I}_7^{2-} + \text{I}^- + 18\text{CO}$. In a typical reaction 7.5 mmol of $[(\text{C}_4\text{H}_9)_4\text{N}]\text{Mo}(\text{CO})_6$, 2.5 mmol of $\text{Mo}(\text{CO})_6$, and 3.75 mmol of I_2 are refluxed under N_2 in 35 mL of chlorobenzene until CO evolution is complete (~ 2 h). After cooling, the black, finely crystalline product is filtered and washed with chlorobenzene until the filtrate becomes colorless. The compound is moderately air sensitive.
- (5) Anal. Calcd: Mo, 16.95; I, 61.64; C, 16.97; H, 3.20; N, 1.24. Found: Mo, 16.85; I, 61.58; C, 17.06; H, 3.22; N, 1.44.
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- (9) In C_{4v} symmetry the M-M bonding in $\text{Mo}_5\text{Cl}_{13}^{2-}$ can be described as $(3a_1 + b_1 + b_2 + e)_{\text{bonding}}(e + e)_{\text{nonbonding}}$. The formally nonbonding pairs of e orbitals are localized on the four basal Mo atoms. In a formal sense these orbitals can be viewed as those generated, one on each basal Mo, when the four bonds are broken upon removal of one Mo from the $\text{Mo}_6\text{X}_8^{4+}$ cluster unit. These e orbitals are formally nonbonding because the LCAO's involve only interactions between Mo atoms located in diagonal corners of the square base.
- (10) In C_{2v} symmetry the M-M bonding in $\text{Mo}_4\text{I}_7^{2-}$ can be described as $(3a_1 + a_2 + b_1 + b_2)_{\text{bonding}}(a_2 + b_1)_{\text{nb}}$. The latter a_2 and b_1 orbitals involve mainly interactions at the distance 3.035 \AA between d orbitals lying in planes perpendicular to the Mo(1)-Mo(2) axis. These orbitals thus should have neither strong bonding or antibonding character.
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- (13) In the planar Nb_4 cluster of $\text{CsNb}_4\text{X}_{11}$ two of the Nb atoms have coordination number 9 ($6\text{Nb-X} + 3\text{Nb-Nb}$) and two have coordination number 8 ($6\text{Nb-X} + 2\text{Nb-Nb}$). The two Nb atoms with coordination number 8 each have an unoccupied nonbonding orbital which could accommodate a total of 4 more electrons. Thus a total of 14 metal-metal electrons might be housed in either bonding or nonbonding MO's. In these compounds the nonbonding orbitals are vacant; addition of electrons to these orbitals would require a large difference in formal oxidation number of the two nonequivalent pairs of Nb atoms.
- (14) The formula of $\text{Mo}_4\text{S}_4\text{Br}_4$ is better written as $\text{Mo}_4\text{S}_4\text{Br}_{12/3}$ which reflects the fact that the cluster units are interconnected by bridging Br atoms. Each Mo thus attains a coordination number 9 ($3\text{Mo-S} + 3\text{Mo-Br} + 3\text{Mo-Mo}$) and it is readily seen that this leads to a closed configuration for the cluster where all bonding MO's are filled and all antibonding orbitals are vacant. In this cluster unit there are no nonbonding orbitals centered on the metal atoms. The Mo-Mo bonding can be described as $(a_1 + e + t_2)$.¹²

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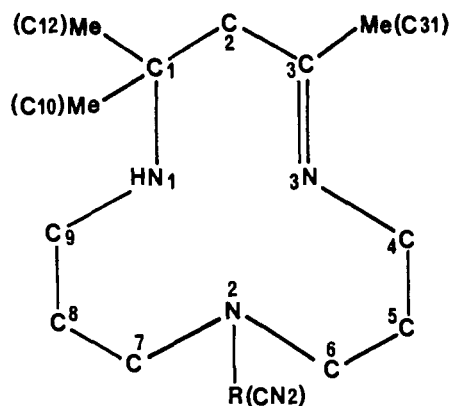
Received May 22, 1978

A Novel Mode of Carbonate Binding. Structure of Spin-Paired μ -Carbonato-bis(2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene)dycopper(II) Perchlorate

Sir:

Partial spin pairing by antiferromagnetic coupling is relatively common for dinuclear Cu(II) compounds,¹ but few examples have been well characterized where complete spin pairing results in diamagnetism.²⁻⁴

The twelve-membered triaza macrocycles L_1 and L_2 form a number of dinuclear compounds with five-coordinate Cu(II), or Ni(II), with di- μ -chloro, di- μ -hydroxo, μ -oxalato, etc.,



L_1 ($R = H$). L_2 ($R = Me$). Crystallographic atom numbering for L_2 is shown.

bridging groups.⁵ Several of the compounds of Cu(II) show subnormal magnetic moments, indicating spin pairing by superexchange via the bridging groups.⁵ One such compound, dark green μ -carbonato-bis(2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene)dycopper(II) perchlorate, $\{[Cu(L_2)]_2CO_3\}(ClO_4)_2$, I, is completely spin paired, showing a small residual temperature independent paramagnetism over the range 100–300 K.⁶

The crystal and molecular structure of $\{[Cu(L_2)]_2CO_3\}(ClO_4)_2$ as a dimethylformamide solvate⁷ has been determined by X-ray diffractometry. Orthorhombic crystals of the compound $\{[Cu(L_2)]_2CO_3\}(ClO_4)_2 \cdot C_3H_7NO$ were grown from dimethylformamide/propan-2-ol: space group $Iba2$; $a = 16.19(1)$, $b = 16.67(1)$, $c = 15.43(1)$ Å; $Z = 4$. Full-matrix least-squares refinement using 1231 observed reflections resulted in an R value of 0.052. The structure of the cation is shown in Figure 1.

The compound has a dinuclear cation with five-coordinate Cu(II) ions linked by a CO_3^{2-} ion, with the CO(1) bond lying along a crystallographic twofold axis which relates the halves of the dimer. The oxygen atom O(1) is bonded to both Cu(II) ions, with CuOCu linear, while the atoms O(2) and O(2)' also bond each to a single Cu(II) ion; thus the symmetrical carbonate ion acts as an asymmetric bidentate ligand to both metal ions.

The coordination geometry about each Cu(II) is distorted square pyramidal, with the tertiary nitrogen atom N(2) in the apical site. The interbasal angles of the square pyramid, $\angle CuX$, in the cyclic sequence O(1), O(2), N(1), N(3) are 65.3, 98.0, 93.9, 96.4°; the apex base angles $\angle N(2)CuX$ in the same sequence are 109.0, 98.5, 105.6, 93.2°, all $\sigma = 0.3^\circ$. The Cu–O distances are similar at 2.041(1) Å for O(1) and 2.028(5) Å for O(2). The Cu–N distance is shorter for the imine nitrogen N(3) at 1.961(7) Å than for the amine nitrogen N(1) at 1.977(7) Å, with the distance to the apical tertiary nitrogen N(2) much longer at 2.195(7) Å. The triaza macrocycle L_2 is coordinated in the same configuration and in a very similar conformation to that observed for L_1 in $Ni(L_1)(NCS)_2$ and the coordination geometry is similar for the two compounds.⁵ The methyl group C(10) is close to the "vacant octahedral site" with Cu–C(10) of 2.95(2) Å; cf. Ni–C(10) of 2.92 Å for $Ni(L_1)(NCS)_2$. The carbonate ion dimensions are as follows: C–O(1), 1.32(1) Å; C–O(2), 1.27(1) Å; O(1)–C–O(2), 116.1(0.5)°; O(2)–C–O(2)', 128(1)°.

The visible spectrum⁸ of I shows d–d bands at 9500 (50) and 15 500 (300) cm^{-1} and a band at 26 800 (5100) cm^{-1} , in the region where many Cu(II) compounds which exhibit antiferromagnetic absorb. The IR spectrum of I shows bands assignable to CO_3^{2-} at 1570, 1350 (ν_3), 830 (ν_2), and 730 (ν_4) cm^{-1} . Separations of this magnitude between the components of ν_3 have been shown by compounds with bidentate and with bridging unidentate coordination.⁹

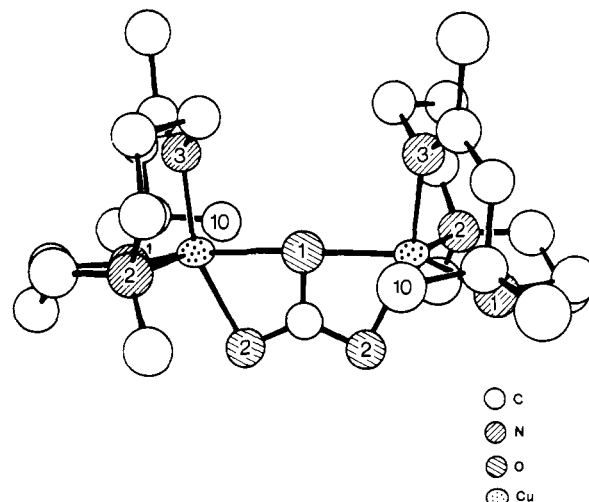


Figure 1. Structure of the cation of $\{[Cu(L_2)]_2CO_3\}(ClO_4)_2 \cdot HCON(CH_3)_2$. The bond C–O(1) lies along a crystallographic twofold axis.

Structural studies have established a variety of types of interaction with metal ions by CO_3^{2-} or NO_3^- , but none analogous to that found for I.^{10–12} The structure most closely related is probably malachite, $Cu(OH)_2CO_3$, where one O of the CO_3^{2-} interacts with two Cu(II) ions, with CuOCu nonlinear, while the other O atoms interact with separate Cu(II) ions in sites of a different type.¹¹

Many structural studies have been reported of Cu(II) compounds which show antiferromagnetic interactions, usually with two bridging atoms, and relationships between the bonding geometry at the bridging atoms and the coupling constants have been established for some of these systems.¹ The one previously reported structural study of a diamagnetic copper(II) compound revealed a structure of this type, with a symmetrical $Cu(O_2)Cu$ bridge.² The structure of I, with a single linear CuOCu bridge, is novel and can be compared with that of the spin-paired anion $[Cl_5RuORuCl_5]^{4-}$ and the "basic rhodo" cation $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ which has much greater spin coupling than the "acid rhodo" cation with a nonlinear $Cr(OH)Cr$ bridge. The linear CuOCu arrangement, with 90° bond angles at the bridging oxygen atom, provides the ideal geometry for antiferromagnetic spin coupling. Other Cu(II) carbonate compounds reported to show antiferromagnetism include the compound $Cu_4(dpt)_4(CO_3)Cl_6 \cdot H_2O$, which shows a subnormal room temperature magnetic moment,¹⁴ and $Cu(NH_3)_2CO_3$, which shows antiferromagnetism below 20 K.¹⁵

Acknowledgment. A.R.D. and F.W.B. thank the National Research Council of Canada for financial support.

Supplementary Material Available: A listing of atom coordinates, thermal parameters, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Received June 1, 1978

Metal-Ammonia Solutions. 11.

Au^- , a Solvated Transition Metal Anion

Sir:

Historically, the chemistry of metals in solution is characterized by their ability to form positive ions. However, stable negative metal ions are well known in the gas phase,¹ liquid CsAu behaves much like other molten ionic salts,² and ammonia solutions of numerous anions of the main group elements are known, e.g., anions such as Pb_9^{4-} .^{3,4} Recently, the existence of alkali metal anions in amine and ether solvents was proven,⁵ although the existence of such species in liquid ammonia is still questionable. Finally, Zintl et al. observed in the potentiometric titration of a sodium-ammonia solution by an AuI-ammonia solution an end point corresponding to 1 equiv of Au^+ added to 2 equiv of Na^0 .⁴ The authors interpreted their data as showing the formation of an "intermetallic phase", although the data could also imply the existence of Au^- . We report here spectroscopic and electrochemical evidence for the first transition metal anion in any solvent, and the first metal anion in ammonia, viz., Au^- .

Solutions of auride ions can be prepared in a number of ways, the simplest of which is the dissolution of metallic gold in ammonia solutions of cesium, rubidium, or potassium. Since dissolution is considerably faster at ambient temperature, much of the spectroscopic work described here was carried out in a cell capable of withstanding the 10-atm vapor pressure of ammonia at that temperature. The apparatus consists of a 1-mm quartz optical cell connected by a graded seal to a Pyrex solution make-up bulb and a pressure stopcock. Portions of solutions in the make-up bulb can be tipped into the optical cell and diluted as required for spectroscopic analysis by distilling ammonia from the solution left in the make-up bulb. By using ratios of absorbances on the broad tail of the solvated electron band before and after dilution, and the weight of gold used, estimates were obtained for the extinction coefficient of Au^- at ambient temperature.

The inability of sodium, lithium, strontium,⁶ or barium⁶ solutions to dissolve gold probably arises from surface effects because a sodium-[2.2.2]-cryptand solution will dissolve gold⁶ and because Au^- can be prepared by using lithium and a method which eliminates surface problems, specifically, cocondensation.

The cocondensation technique as used in this investigation involves the simultaneous vacuum vaporization of lithium and gold and their subsequent cocondensation along with gaseous ammonia onto a liquid nitrogen cooled surface. Warming the

resultant matrix to the melting point of ammonia produces solutions of Au^- . The present apparatus is similar to one described elsewhere,⁷ except that this one is constructed completely of quartz and has two optical windows spaced 0.3 and 10 mm apart attached to the bottom. This cell was also used for the spectroscopic experiments conducted below the boiling point of ammonia, even if cocondensation was not required.

The spectroscopic evidence for the existence of Au^- in liquid ammonia is illustrated by the results of a typical experiment conducted at ambient temperature. A 2×10^{-2} M cesium-ammonia solution dissolved sufficient gold to make a 3×10^{-3} M cesium auride solution. Absorption bands at 289 and 356 nm increased in intensity as the gold dissolved. After complete dissolution, the solvated electrons continued to decompose (by reaction with the solvent to form amide), the 356-nm band continued to increase, but the intensity of the 289-nm band remained constant. A partially decomposed cesium-ammonia solution also showed the 356-nm band; furthermore, rubidium and potassium solutions each have a similar band, the positions of which are in agreement with those for the respective amides published elsewhere.⁸ When the broad solvated electron band at 1850 nm had virtually disappeared, concentration of the solution by evaporation of the solvent caused pure metallic gold to precipitate, as did freezing the solution. The intensity of the 289-nm band decreased during these processes.

Similar experiments show an absence of other bands in gold-containing solutions; bands with extinction coefficients >25 could have been detected. The cocondensation of gold with ammonia produces a solution which contains only a black precipitate of gold. Yet the triple cocondensation of lithium and an excess of gold with ammonia still produces the Au^- band, but no solvated electrons, demonstrating that Au^- is stable even in the absence of solvated electrons.

Solutions of gold with cesium, rubidium, and potassium at ambient temperature all exhibit the Au^- band at 289 nm. At -65°C this band occurs at 277.1 nm in the case of a Cs-CsAu solution and at 278.4 nm for a LiAu solution. Yet the temperature coefficients for the two solutions (determined from data at temperatures less than the boiling point of ammonia) are identical, $-18\text{ cm}^{-1}/\text{deg}$. This difference in peak position is small (cf. CsNH_2 and LiNH_2 at 327.5 and 298.0 nm, respectively⁸) but real.

The large temperature coefficient is one distinguishing characteristic of a charge-transfer-to-solvent transition; another is a large extinction coefficient.⁹ For the slightly asymmetric auride band, the extinction coefficient is estimated at $5 \times 10^4\text{ L}/(\text{mol cm})$ at -65°C and $7 \times 10^4\text{ L}/(\text{mol cm})$ at ambient temperature. For comparison, other anions which exhibit charge-transfer-to-solvent transitions in ammonia, i.e., e^-_{am} , I^- , and NH_2^- , exhibit extinction coefficients of $4.5 \times 10^4\text{ L}/(\text{mol cm})$ at -65°C ,¹⁰ $1.8 \times 10^4\text{ L}/(\text{mol cm})$ at -78°C ,¹¹ and $3.48 \times 10^3\text{ L}/(\text{mol cm})$ at -49°C ,¹² respectively, and temperature coefficients of $-10\text{ cm}^{-1}/\text{deg}$,^{10,13} $-22\text{ cm}^{-1}/\text{deg}$,¹¹ and $-17\text{ cm}^{-1}/\text{deg}$.¹²

The chemical behavior of the gold solutions and the large extinction and temperature coefficients of the gold-related band indicate the presence of a solvated gold anion. To further confirm our assignment, preliminary electrochemical experiments were undertaken.

The electrochemical cell used was a standard three-compartment cell described elsewhere.^{14,15} A silver wire was used as a pseudoreference electrode and a platinum disk as the working electrode. Solvated electrons were generated coulometrically,¹⁵ using 0.1 M CsI as a supporting electrolyte. Metallic gold was then introduced into the solution and allowed to dissolve. A potential scan starting at -2.6 V showed an anodic wave at -2.1 V and upon reversal a cathodic wave at -2.5 V , demonstrating that the species in solution is oxidized at a potential nearly that of the solvated electron's.