

models reveals no interaction between the *N*-methyl and *C*-methyl groups in sarcosyl-L-alanine. Therefore the distribution of *N*-methyl groups might be equal above and below the chelate plane, effecting a cancellation of any contribution to the optical activity from this source provided the contributions of *N*- and *C*-methyl groups are additive. The results for the first two compounds of Table III indicate that the situation is somewhat more complicated than the simple suggestion. Complexes of Cu(II) with but two nitrogen and two oxygen donors appear to require at least a fifth ligand in an apical position.⁷ A water molecule in the fifth

position might favor the situation where both methyl groups of sarcosyl-L-alanine lie on the same side of the Cu(II) chelate plane opposite that of the water molecule. Any effects ascribable to a fifth ligand in a Cu(II) complex should be diminished or absent in the corresponding more strongly tetragonal Pd(II) complex.

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Copper(III) and Nickel(III) Complexes of Biuret and Oxamide

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Bis-biuretato complexes of Cu(II) and Ni(II) $K_2M(Rbi)_2$ (where M is Cu or Ni, and Rbi is the dianion $HNCONRCONH$ formed by deprotonation of the corresponding biuret, R = H or alkyl) can be oxidized to $KM(Rbi)_2$ in which the metal has the oxidation number III. Nmr, ir, and magnetic susceptibility studies of these compounds revealed that these ligands are bonded *via* their N atoms, most probably in a planar coordination around the metal. The oxidation occurs in aqueous solutions at a potential of 0.50–0.65 V (relative to a saturated calomel electrode); in DMSO the reaction is a reversible one-electron transfer at $E_{1/2} = -0.35$ V as was shown by polarographic measurements. Two H_2O or $RbiH_2$ molecules can be bonded to the coordinated biuretate groups, most probably *via* H bridges. A bis-oxamidato complex $KCu(HNCOCONH)_2$ could be prepared with analogous properties. The stabilizing influence of these ligands on the high oxidation states of the metals is thought to be due to the very strong electron-donating capacity of the deprotonated amine groups.

Introduction

In a previous short communication¹ we have reported the preparation and the properties of bis-biuretato complexes of Cu(III) and Ni(III) with compositions of $KCu(bi)_2$ and $KNi(bi)_2$, respectively, wherein bi is the dinegative ion $HNCONHCONH$ formed by deprotonation of biuret ($H_2NCONHCONH_2 = biH_2$). The further study of these compounds was seriously hampered by their extremely low solubility. We now succeeded in preparing analogous complexes derived from the alkyl-substituted biuretate ions (of the type $HNCONRCONH$) which are soluble in acetone, alcohol, and DMSO, allowing a more detailed study. With respect to the oxidation to a Cu(III) complex the dianionic form of oxamide ($HNCOCONH = oxam$) behaves in the same way as the biuretate ion. We shall report here about the preparation and the properties of these compounds in which Cu and Ni have the uncommon oxidation state III. The specific influence of the ligands leading to a stabilization of these high oxidation states will be discussed.

Experimental Part

$K_2Cu(bi)_2$, $K_2Ni(bi)_2$, and $K_2Cu(oxam)_2$ were prepared according to known methods.^{2,3}

Preparation of $KCu(bi)_2$.—(a) A solution of $K_2Cu(bi)_2$ was prepared by dissolving 2.2 g of biuret, 2.5 g of $CuSO_4 \cdot 5H_2O$, and

3 g of KOH in 25 ml of water. When an excess of $K_2S_2O_8$ was added to this solution, the compound $KCu(bi)_2$ precipitated immediately. The compound was filtered off, washed with hot water (70°), and dried in a vacuum desiccator.

(b) When the above-mentioned $K_2Cu(bi)_2$ solution was electrolyzed between Pt electrodes, $KCu(bi)_2$ was precipitated on the anode. The anode potential, measured with an auxiliary saturated calomel electrode, was 0.50 V. The compound was collected, washed with water, and dried.

(c) $KCu(bi)_2$ was formed when air with some hydrogen chloride was bubbled through a suspension of $K_2Cu(bi)_2$ in benzene. On further study, uv irradiation, formerly reported to be necessary,¹ appeared to be redundant.

Anal. Calcd for $KCu(bi)_2$: Cu, 20.85; K, 12.84; C, 15.76; H, 1.97; N, 27.58. Found: Cu, 20.95; K, 12.72; C, 15.61; H, 2.02; N, 27.25 (for a sample prepared according to method a, the other methods give analogous results).

Preparation of $KNi(bi)_2$.—The procedures a and b, as described for $KCu(bi)_2$, but now starting with $NiSO_4$, were possible. Method b gave a very poor yield. The electrode potential, measured relative to saturated calomel electrode was 0.50 V. Preparation according to procedure c was impossible. *Anal.* Calcd for $KNi(bi)_2$: Ni, 19.57; K, 13.04; C, 16.02; H, 2.02; N, 28.01. Found: Ni, 19.60; K, 13.10; C, 16.22; H, 2.13; N, 27.25.

Preparation of $KCu(Rbi)_2 \cdot 2H_2O$.—The preparation of pure 3-alkylbiuret appeared to be very difficult. The recipe of Weith⁴ for the preparation of 3-phenylbiuret, modified to produce 3-alkylbiuret, yielded a mixture of products, among which were 3- and 1-alkylbiuret. The separation of 3-alkylbiuret was very difficult and will be published elsewhere. In the next sections we give methods to prepare $KCu(3-Rbi)_2 \cdot 2H_2O$, R = propyl, starting with pure 3-propylbiuret and with the just mentioned reaction mixture.

(a) When 1 g of KOH was added to a solution of 0.5 g of $CuSO_4 \cdot 5H_2O$ and 1 g of 3-propylbiuret in 10 ml of water, Cu-

(1) J. J. Bour and J. J. Steggerda, *Chem. Commun.*, **2**, 85 (1967).

(2) H. C. Freeman, J. E. W. L. Smith, and J. C. Taylor, *Acta Crystallogr.*, **1**, 407 (1961).

(3) M. M. Rising, J. S. Hicks, and G. A. Moerke, *J. Biol. Chem.*, **1**, 1 (1930).

(4) W. Weith, *Ber.*, **10**, 1844 (1877).

(3-Rbi)₂²⁻ was formed. By electrolytic oxidation of this solution, KCu(3-Rbi)₂·2H₂O precipitated on the platinum anode (anode potential 0.50 V relative to the saturated calomel electrode). The product was rinsed with water, dried, and dissolved in acetone. After evaporation of the acetone, the complex was crystallized from an alcohol or DMSO solution by adding chloroform and ether.

(b) With this same procedure but using the above-mentioned reaction mixture of 1- and 3-propylbiuret (instead of pure 3-propylbiuret), the interesting product KCu(3-Rbi)₂(1-RbiH₂)₂ was obtained. If a DMSO solution of this complex was exposed to moist air for 24 hr, KCu(3-Rbi)₂·2H₂O could be precipitated by adding chloroform and ether. The preparation by oxidation of K₂Cu(3-Rbi)₂ with K₂S₂O₈ or with air was not possible.

Anal. Calcd for KCu(3-Rbi)₂(1-RbiH₂)₂: Cu, 9.35; K, 5.76; C, 35.36; H, 5.94. Found: Cu, 9.29; K, 5.92; C, 34.50; H, 6.40. Calcd for KCu(3-Rbi)₂·2H₂O: Cu, 14.95; K, 9.20; C, 28.26; H, 5.22. Found: Cu, 14.90; K, 9.10; C, 28.15; H, 5.23.

Preparation of KNi(3-Rbi)₂(1-RbiH₂)₂.—The same procedure as for the corresponding Cu complex could be used. The electrode potential was 0.65 V (relative to sce). Because the yield was very poor, the product could only be identified by its ir spectrum being identical with that of the analogous Cu complex.

Preparation of KCu(oxam)₂.—By electrolytic oxidation of a slurry of 3 g of oxamide in a solution of 1 g of K₂Cu(oxam)₂ in 50 ml of 0.1 N KOH (electrode potential of 0.55 V (relative to sce), KCu(oxam)₂ precipitated as a yellow product on the anode. The product could be purified from coprecipitated copper oxide by rinsing it fast with 1 N HCl, which dissolved the copper oxide much faster than the KCu(oxam)₂. The complex was decomposed when exposed to light. *Anal.* Calcd for KCu(oxam)₂: Cu, 23.12; C, 17.49; H, 1.49; N, 20.39. Found: Cu, 23.01; C, 17.40; H, 1.48; N, 20.95. The preparation of the corresponding Ni complex appeared to be impossible.

Physical Measurements.—Magnetic susceptibilities were measured at room temperature using a standard Gouy-type balance. The results are given in Table I. Polarographic data were obtained with a Metrohm Polarecord E 261. DMSO was used as solvent with 0.05 M (n-C₄H₉)₄NCIO₄ as supporting elec-

TABLE I
MAGNETIC DATA AT 25°, AFTER CORRECTION FOR DIAMAGNETISM
ACCORDING TO FIGGIS AND LEWIS^a

| | Molar susceptibility × 10 ⁴ , cgsu | Effective magnetic moment, BM |
|---|--|-------------------------------|
| KCu(bi) ₂ | 10 | Diamagn |
| KNi(bi) ₂ | 2600 | 2.5 |
| KCu(3-Rbi) ₂ ·2H ₂ O | 180 | Diamagn |
| KCu(3-Rbi) ₂ (1-RbiH ₂) ₂ | 230 | Diamagn |
| KCu(oxam) ₂ | 200 | Diamagn |

^a I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Part I, Vol. 4, Interscience, New York, N. Y., 1963, pp 1778-1781.

TABLE II
POLAROGRAPHIC DATA IN DMSO SOLUTIONS
(DME RELATIVE TO SCE)

| | E _{1/2} , V | Slope, ^a mV |
|---|----------------------|------------------------|
| RCu(3-Rbi) ₂ (1-RbiH ₂) ₂ | -0.35 | 65 (reduction wave) |
| KCu(3-Rbi) ₂ ·2H ₂ O | -0.36 | 58 (reduction wave) |
| K ₂ Cu(3-Rbi) ₂ | -0.33 | 54 (oxidation wave) |

^a Slope of the plot of log [i/(i_a - i)] vs. E, which for a reversible one-electron transfer at 25° is 58 mV.

100 MHz. As external reference HMDS was used. The relevant nmr data are given in Table IV. Due to their insolubility no nmr spectra could be taken of the unsubstituted biuretato and oxamidato complexes. The data of the electronic spectra, measured with a Zeiss PMQ II spectrophotometer, are given in Table V.

Results and Discussion

The oxidation of the biuretato complexes of Cu(II) and Ni(II) to the respective Cu(III) and Ni(III) compounds and of the Cu(II) oxamidato to the copper(III)-oxamidato complex is possible in alkaline solutions at oxidation potentials of 0.7-0.9 V. This is

TABLE III
C=O STRETCHING FREQUENCIES (CM⁻¹)

| K ₂ Cu(bi) ₂ ^a | KCu(bi) ₂ | K ₂ Ni(bi) ₂ ^a | KNi(bi) ₂ | K ₂ Cu(oxam) ₂ | KCu(oxam) ₂ |
|---|--|---|----------------------|--------------------------------------|------------------------|
| 1630 | 1695 | 1635 | 1695 | 1620 | 1670 |
| 1565 | 1590 | 1570 | 1615 | 1590 | 1645 |
| KCu(3-Rbi) ₂ (1-RbiH ₂) ₂ | KCu(3-Rbi) ₂ ·2H ₂ O | KNi(3-Rbi) ₂ (1-RbiH ₂) ₂ | 3-RbiH ₂ | 1-RbiH ₂ | |
| 1720 | | 1720 | 1715 | 1720 | |
| 1690 | | 1690 | 1690 | 1690 | |
| 1615 | 1615 | 1650 | | | |
| 1580 | 1580 | 1580 | | | |

^a B. B. Kedzia, P. X. Armendarez, and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **30**, 849 (1968). ^b P. X. Armendarez and K. Nakamoto, *Inorg. Chem.*, **5**, 796 (1966).

TABLE IV
¹H NMR DATA OF THE COPPER-BIURETATO COMPLEXES AND THEIR LIGANDS^a

| ^b | CH ₃ | CH ₂ | N-CH ₂ | N ₁ < ^{Cu} H | N ₁ H ₂ | N ₁ HR | N ₃ H |
|---|-----------------------|-----------------|-------------------|-------------------------------------|-------------------------------|-------------------|------------------|
| Biuret | | | | | 3.06 (4) | | 1.28 (1) |
| 1-Rbi | 8.94 (3) ^c | 8.36 (2) | 6.77 (2) | | 3.11 (2) | 2.36 (1) | 1.30 (1) |
| 3-Rbi | 8.96 (3) | 8.32 (2) | 6.28 (2) | | 2.56 (4) | | |
| KCu(3-Rbi) ₂ (1-RbiH ₂) ₂ | 8.96 (6) | 8.40 (4) | 6.77 (2) | 6.36 (2) | 4.42 (2) | 3.06 (2) | 2.29 (1) |
| KCu(3-Rbi) ₂ ·2H ₂ O | 9.00 (3) | 8.42 (2) | 6.36 (2) | 4.40 (2) | | | |

^a R = CH₃CH₂CH₂. Nitrogen atoms are numbered according to the structure >N₂-C(=O)-N₃-C(=O)-N₁<. ^b τ = 10 + [(H_{comp} - H_{ref})/H_{ref}](10°) (H = field strength; comp = measured compound; ref = reference). ^c The intensity ratios of the bands are given in parentheses.

trolyte. The potentials of the dropping mercury electrode were measured relative to a saturated calomel electrode. The data are listed in Table II. Infrared spectra of the solid compounds in KBr pellets were measured with a Perkin-Elmer 157 instrument. The C-O stretching frequencies are listed in Table III. Nmr spectra in hexadeuteriodimethyl sulfoxide solutions were measured with a Varian HA 100 instrument operating at

in agreement with the results of Levitzki and Anbar,⁵ who estimated the oxidation potential of the reaction Cu(bi)₂²⁻ → Cu(bi)₂⁻ + e⁻ to be between 0.85 and 1.07 V. These high potentials are about the limit

(5) A. Levitzki and M. Anbar, *Chem. Commun.*, 403 (1968).

TABLE V
 ELECTRONIC SPECTRAL DATA (CM⁻¹)^a

| | | | | | | Solvent |
|---|-----------------|---------------|--------------|-------------|--|------------------------------|
| K ₂ N(bi) ₂ | 46,500 (18,500) | | 24,400 sh | 21,700 (51) | | 0.1 N KOH |
| KCu(bi) ₂ | 41,000 s | 29,400 vs | 21,700 w, sh | 17,200 sh | | BaSO ₄ reflection |
| KCu(3-Rbi) ₂ (1-RbiH ₂) ₂ | 37,000 (5000) | 26,800 (8000) | 20,400 w, sh | 17,500 sh | | DMSO |
| KCu(3-Rbi) ₂ ·2H ₂ O | 37,000 (5000) | 26,800 (8500) | 20,400 w, sh | 17,500 sh | | DMSO |
| K ₂ Ni(oxam) ₂ | 29,000 s | 28,000 s | 22,500 sh | | | 0.1 N KOH |
| KCu(oxam) ₂ | 28,700 s | 27,000 s | 22,600 sh | 19,800 sh | | BaSO ₄ reflection |
| KNi(bi) ₂ | 43,900 m | 33,100 m | 18,500 sh | 15,000 s | | BaSO ₄ reflection |

^a Extinction coefficients are given in parentheses. Abbreviations: vs, very strong; s, strong; m, medium; sh, shoulder; wsh, weak shoulder.

of what is possible in aqueous alkaline solutions. Slight modifications in the ligands cause the synthesis to fail; despite considerable effort, we did not succeed in preparing the oxamidato complex of Ni(III) and 3-phenylbiuretato and malondiamidato complexes of Cu(III) and Ni(III). We think that the specific influence of the biuretato and oxamidato ligands is primarily due to the strong electron-donating power of the deprotonated amine groups in these ligands. These cause a very high electron density on the metal ion, facilitating its oxidation. The Cu compounds are more easily oxidized than those of Ni. The base strength of the ligands required for a stable oxidation product must be between an upper and a lower limit. When the base strength of the anion is very high, no deprotonation of the amine can occur; below a certain base strength the oxidation is impossible. Obviously the limits are also dependent on the redox as well as on the acidic properties of the solvent. Due to solubility problems however no other solvent than water could be investigated. Most amines, aliphatic or aromatic, are too weak acids to deprotonate, even in strongly alkaline solutions. The neighboring C-O groups in biuret and oxamide apparently give a situation just between the critical limits. The failure to prepare the 3-phenylbiuretato complexes of Cu(III) and Ni(III) must then be ascribed to the electron-withdrawing capacity of the phenyl groups, which decrease the base strength of the ligand below the critical value for which oxidation of the metal is possible. Although deprotonation and complexation of malondiamide to Cu(II) was demonstrated by Rising, Hicks, and Moerke,³ the impossibility to oxidize that complex is probably due to the lack of π delocalization, which certainly also contributes to the stability of the biuretato and oxamidato compounds.

Nmr spectra of the copper-biuretato complexes show them to be coordinated *via* the N atoms (see Table III). This same can be concluded from the ir spectra of all Cu(III) and Ni(III) complexes, using the criterion given by McLellan⁶ and Kedzia.⁷ The oxamidato complexes of Cu(II) and Ni(II) are coordinated *via* N atoms as was established by the interpretation of ir spectra.⁸ Since the ir spectrum of KCu(oxam)₂ resembles closely that of K₂Cu(oxam)₂, we think their structures to be similar (see Figure 1). X-Ray crystal work has shown that the bis-biuretato complex of Cu(II) is planar.² For the bis(biuretato)-nickel(II) complex planarity was concluded on the basis of the diamagnetism and ir and electron spectroscopic

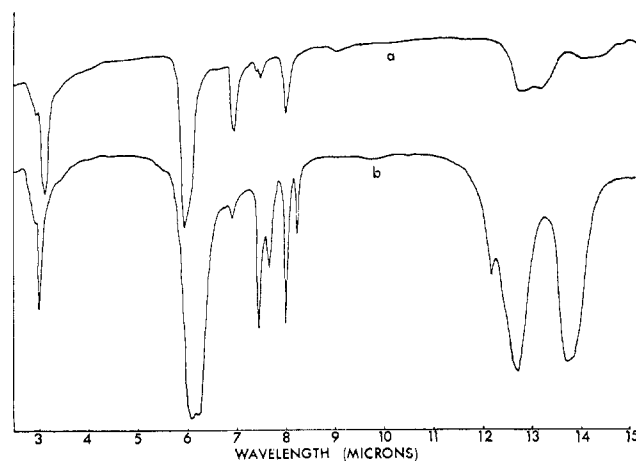


Figure 1.—Ir spectra of (a) KCu(oxam)₂ and (b) K₂Cu(oxam)₂ in the 3–15- μ region.

data.⁶ A detailed study of the ir spectra of the oxamidato complexes of Cu(II) and Ni(II) points out a planar structure for these compounds.⁸ We think the newly prepared Cu(III) and Ni(III) complexes also to be planar, a conclusion mainly based on the observed magnetic data, the Cu(III) complexes being diamagnetic and the Ni(III) complexes paramagnetic according to one unpaired electron spin.

The polarographic half-wave potentials of the oxida-

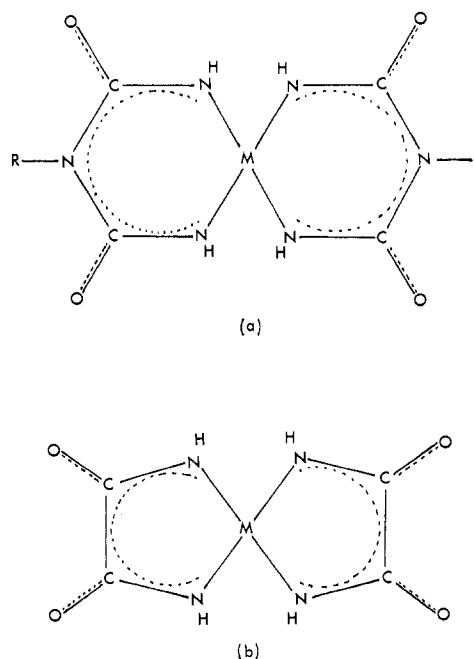


Figure 2.—The proposed planar structures of the biuretato (a) and oxamidato (b) complexes.

(6) A. W. McLellan and G. A. Melson, *J. Chem. Soc. A*, 137 (1967).

(7) B. B. Kedzia, P. X. Armendarez, and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **30**, 849 (1968).

(8) P. X. Armendarez and K. Nakamoto, *Inorg. Chem.*, **5**, 796 (1966).

tion and reduction waves of the Cu(III) and Cu(II) compounds, respectively, are practically identical. This fact, as well as the observed linearity of the log $[i_d - i]$ vs. E plot, reveals that both compounds can be interconverted by a reversible one-electron step (i_d = diffusion current). This reversibility strongly suggests that both complexes have very similar structures, viz., planar four-coordination as illustrated in Figure 2.

The data of the electronic spectra of $\text{KCu}(\text{bi})_2$ and $\text{KCu}(\text{oxam})_2$, together with those of the isoelectronic Ni(II) species, are given in Table V. This similarity in these spectra give support to the idea of the structural similarity of these compounds. Regarding the structure of the Ni(III) complexes, however, no more evidence is available at the moment.

From a structural point of view these compounds are thus much like the series of MN_4^n complexes reported by Balch and Holm.⁹ The ligand in these series (where n can vary from 2- to 2+) is *o*- $\text{C}_6\text{H}_4(\text{NH})_2$, which can exist in two forms of different oxidation state, viz., as the dianion of *o*-phenylenediamine and as *o*-benzoquinonediimine. This fact is strongly related to the characteristic properties of these series of metal complexes. Since different oxidation forms

(9) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).

of the dianions of biuret and oxamide are obviously not possible, we think them to be representatives of a different class of ligands.

The structure of the interesting compounds $\text{KM}(\text{3-Rbi})_2(\text{1-RbiH}_2)_2$ is not definitely established. Nmr data (see Table IV) and ir spectra show that the 1-propylbiuret is not deprotonated and not coordinated to the metal. The identical uv spectra and magnetic properties of $\text{KCu}(\text{3-Rbi})_2 \cdot 2\text{H}_2\text{O}$ and $\text{KCu}(\text{3-Rbi})_2(\text{1-RbiH}_2)_2$ indicate also that there is no coordination of 1-Rbi or H_2O to the Cu. Extensive H bridging is a characteristic feature of the chemistry of the biurets so we think that the two 1-propylbiuret molecules are H bonded to the biuretato ligands, probably *via* the 3-NH groups, because when these places are blocked by substituting an alkyl group, no extra biurets are found to be bonded to the complexes. The two H_2O molecules in $\text{KCu}(\text{3-Rbi})_2 \cdot 2\text{H}_2\text{O}$ are probably bonded in the same way.

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Preparation and Identification of Intermediate Carbonyls of Nickel and Tantalum by Matrix Isolation¹

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All four carbonyls of nickel, $\text{Ni}(\text{CO})_{1-4}$, and possibly six carbonyls of tantalum, $\text{Ta}(\text{CO})_{1-6}$, have been identified *via* infrared spectra in argon matrices at 4.2°K. The carbonyls are prepared by the vaporization of the metal atoms and condensation into a CO-argon mixture. C^{18}O was also used in the identification. Careful warming of the matrix results in the growth and disappearance of ν_{CO} bands in the 2000- cm^{-1} region. In the nickel experiments these bands appear at 2052, 2017, 1967, and 1996 cm^{-1} and are assigned to $\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{CO})_3$, $\text{Ni}(\text{CO})_2$, and NiCO , respectively. Specific assignments for tantalum carbonyls are more difficult, but five or six molecules are definitely formed during the diffusion experiments. For the tantalum carbonyls also, the general trend is that the stretching frequencies increase with increasing coordination number, a fact which is predicted on the basis of simple bonding theory. In the electronic spectra broad absorptions at 3000 and 2725 Å are attributed to $\text{Ni}(\text{CO})_4$ and $\text{Ta}(\text{CO})_6$, respectively.

Introduction

The matrix isolation technique is ideally suited for the study of unstable species. Such species can include radicals such as HNO^3 or transition metal oxides such as WO and WO_2 .⁴ It is also possible to prepare molecules within the matrix that may be quite stable under ambient conditions; for example, KrF_2 is prepared by the photolysis of fluorine in a krypton matrix.⁵ Another example of the preparation of unique

species is the identification of $(\text{SiO})_2$ and $(\text{SiO})_3$ formed by annealing matrices containing SiO .⁶ Recently, Timms⁷ has presented an approach to the preparation of macro quantities of compounds by allowing the "matrix" material to be a reactant. One of the reactions carried out is the cocondensation of nickel atoms with a solid layer of PF_3 at 77°K to form $\text{Ni}(\text{PF}_3)_4$.

Carbon monoxide has been found to be a particularly reactive molecular species at low temperature. For example, CCO has been prepared by the photolysis of N_3CN in an Ar-CO matrix,⁸ while HCO can be

(1) Support from the National Science Foundation under Grant No. GP-9316 is gratefully acknowledged.

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