Notes

Contribution from the William Albert Noyes
Laboratory of Chemistry,
University of Illinois, Urbana, Illinois

Reactions of Tetramethylene Sulfoxide with Copper(II) and Palladium(II) Halides[1,2]

By Devon W. Meek, William E. Hatfield, R. S. Drago, and T. S. Piper[3]

Received February 10, 1964

The preparation and characterization of some copper and palladium complexes of tetramethylene sulfoxide (TMSO) are reported. During the course of the work, some interesting reactions of the complexes were discovered.

Experimental

Preparation of the Complexes. **$Cu_3(C_4H_8SO)_4Cl_6$.**—To 2.0 g. (0.0148 mole) of anhydrous cupric chloride dissolved in 40 ml. of absolute ethanol was added 5 ml. of tetramethylene sulfoxide. A brown complex precipitated immediately from the green solution. The solid was filtered, washed with ether, and dried with an air stream which had been dried with P_4O_{10}.

Anal. Calcd. for $Cu_3(C_4H_8SO)_4Cl_6$: C, 23.43; H, 3.93; Cl, 25.94. Found: C, 23.67; H, 4.04; Cl, 25.35.

$CuCl_2 \cdot C_4H_8SO$.—Three grams of the above complex dissolved in a mixture of 20 ml. of acetone and 20 ml. of absolute ethanol to produce a green solution. A light tan solid precipitated upon boiling the solution for 10 min. The solid was filtered, washed with acetone and ether, and dried with a stream of dry air. The isolated material (2.4 g.) corresponded to 80% of the original complex. Quantitative isolation of the compound $CuCl_2 \cdot C_4H_8SO$ would correspond to 87% by weight of the original; however, the resulting filtrate remained a light green color, so isolation was not quantitative.

Anal. Calcd. for $CuCl_2 \cdot C_4H_8SO$: C, 20.15; H, 3.38; Cu, 26.63. Found: C, 20.48; H, 3.58; Cu, 27.00.

$Cu_3(C_4H_8SO)_4Br_6$.—Three ml. of tetramethylene sulfoxide was added while stirring to a solution of 3.0 g. (0.0135 mole) of anhydrous cupric bromide in 25 ml. of absolute ethanol. Black crystals precipitated almost immediately. The extremely hygroscopic crystals were filtered, washed with anhydrous ether, and dried.

Anal. Calcd. for $Cu_3(C_4H_8SO)_4Br_6$: C, 17.68; H, 2.97; Cu, 17.53. Found: C, 17.44; H, 2.99; Cu, 17.34.

$CuBr_2 \cdot C_4H_8SO$.—A 1.5-g. sample of the above bromide compound dissolved readily in 30 ml. of an equal mixture of acetone and ethanol. Heating the resulting solution at 56° for 10 min. produced metallic gray mica-like platelets with the simultaneous liberation of a volatile lacrimatory compound, probably bromoacetone.

Anal. Calcd. for $CuBr_2 \cdot C_4H_8SO$: C, 14.67; H, 2.46. Found: C, 14.46; H, 2.37.

$PdCl_2 \cdot (C_4H_8SO)_2$.—Palladium chloride (0.015 mole) was dissolved in 10 ml. of warm TMSO. The solution was filtered and cooled overnight at 5°. The brown crystals that resulted were filtered, washed with ether, recrystallized from an equal volume mixture of absolute ethanol and chloroform, and dried.

Anal. Calcd. for $PdCl_2 \cdot 2C_4H_8SO$: C, 24.91; H, 4.18. Found: C, 24.99; H, 4.17.

$PdCl_2(C_4H_8S)_2$.—TMSO (8 ml.) was added to 1.86 g. (0.015 mole) of $PdCl_2$ dissolved in 100 ml. of hot acetone saturated with anhydrous HCl. The solution became dark red on stirring for 15 hr. Addition of 500 ml. of low-boiling petroleum ether caused an oil to separate. The red crystals which formed after the solution sat 3 days at 5° were filtered, washed with ether, and dried. The compound was recrystallized twice from an equal mixture of chloroform and ethanol. Large red flakes formed slowly at 0°. These were washed with ether and dried; yield 75%.

Anal. Calcd. for $PdCl_2 \cdot 2C_4H_8S$: C, 27.17; H, 4.56; Cl, 20.05. Found: C, 27.37; H, 4.83; Cl, 20.52. The infrared spectra of the compound in chloroform and Nujol did not contain the band due to the S–O stretching vibration in the 1150–900 cm.$^{-1}$ region.

Characterization of the Compounds. Spectra.—The infrared spectra were obtained in nitromethane solutions and on Nujol mulls of the solids, using a Perkin-Elmer Model 21 infrared spectrometer with sodium chloride optics. The instrument was frequency calibrated. The results are contained in Table I.

Conductance and Molecular Weight.—The insolubility of $CuCl_2 \cdot TMSO$ in suitable solvents precluded the investigation of the molecular weight, conductivity, and dipole moment.

Magnetic Susceptibility Determinations.—The magnetic susceptibilities were measured and interpreted as previously described.[4]

X-Ray Powder Patterns.—The powder patterns of $CuCl_2 \cdot TMSO$ and $3CuCl_2 \cdot 4TMSO$, obtained with copper K radiation using a Debye–Scherrer camera, are different from one another. That the samples were not contaminated by copper chloride was indicated by the absence of lines corresponding to *d* values of 5.70, 3.42, 2.90, and 2.36 Å.

Results and Discussion

Interpretation of the infrared spectra of the dimethyl sulfoxide complexes proved to be complicated because of the coupling of the S–O stretching frequency with the methyl rocking frequency.[5] The existence of this coupling was subsequently confirmed in dimethyl sulfoxide by a normal coordinate analysis.[6]

Use of the cyclic tetramethylene sulfoxide eliminated the complication of the rocking frequency of the alkyl group and has permitted the unambiguous assignment of the S–O stretching frequency in the TMSO complexes. As with the DMSO complexes, the infrared spectra of several TMSO complexes (Table I) indicate that all the metals studied coordinate with the sulfoxide *via* the oxygen atom, except Pd(II), where sulfur bonding occurs. Platinum(II) is reported to coordinate also *via* the sulfur atom in TMSO.[7] The change in the position of the S–O stretching vibration for the TMSO–copper complexes, compared to uncomplexed TMSO, appears larger than for the corresponding DMSO complexes. This is an interesting example of a system in which it would be incorrect to infer the relative magnitude of the DMSO and TMSO interactions with the metal ion on the basis of

---

[1] The authors wish to acknowledge the financial assistance of the Atomic Energy Commission (Contract No. AT(11-1)-758).

[2] Abstracted in part from the Ph.D. thesis of D. W. Meek, University of Illinois, 1961.

[3] Alfred P. Sloan Foundation Fellow.

[4] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

[5] R. S. Drago and D. W. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).

[6] W. D. Horrocks, Jr., and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).

[7] R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).

TABLE I

MAJOR INFRARED ABSORPTIONS OF TETRAMETHYLENE SULFOXIDE COMPLEXES (CM.$^{-1}$)

Compound	Solvent or mull	Assignments									
		CH stretch	CH_2 deformations						S=O[a]		C—S
C_4H_8SO	CCl_4 (15%)	2930, 2860	1447	1411	1303	1271	1147	1097	1035	875	730
$PdCl_2 \cdot 2TMSO$	KBr	2930	1446	1398	1307	1260	...	1074	1119	875	...
$[Co(TMSO)_6]I_2$	Nujol	2930, 2860	1445	1406	1307	...	1146	1102	947	...	717
$[Co(TMSO)_6][CoCl_4]$	Nujol–HCBD		1445	1408	1304	...	1140	1095	937	...	717
$3CuBr_2 \cdot 4TMSO$	KBr	2980, 2910	1445	1408	1302	1250	...	1104	937	875	...
$CuBr_2 \cdot TMSO$	Nujol–HCBD		1426	1393	1300	...	...	...	925	870	715
$3CuCl_2 \cdot 4TMSO$	Nujol–HCBD		1448	1409	1302	...	...	1107	933	...	714
$CuCl_2 \cdot TMSO$	KBr		1445	1407	1303	1250	...	1104	941	876	...

[a] This band is by far the most intense one of the entire spectrum in each case.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA

Compound	$\chi_M \times 10^6$, c.g.s. units	T, °K.	μ_{eff}, B.M.
$CuCl_2 \cdot TMSO$[a]	1409	325.5	1.90[c]
	1560	297.8	
	1742	273.8	
	2624	194.7	
	8416	80.7	
$3CuCl_2 \cdot 4TMSO$[b]	4302	298.0	1.90[c]
	7100	195.5	
	20,347	80	

[a] The diamagnetic correction is 120 × 10^{-6} c.g.s. unit. [b] The diamagnetic correction is 421 × 10^{-6} c.g.s. unit. [c] Average magnetic moment per copper ion.

the magnitude of the infrared frequency shift. The ligand field *Dq* values for these two ligands are identical for Co(II), Ni(II), and Cr(III).[8] Such a correlation of the shift of the S–O vibration in dimethyl sulfoxide is complicated by coupling with the methyl rocking frequency

The reactions which occur when the compounds of general formula $3CuX_2 \cdot 4TMSO$ are heated in ethanol and acetone are interesting and have not been observed when the DMSO complexes are treated under similar conditions. New compounds of general formula $CuX_2 \cdot TMSO$ are formed from this reaction. The infrared spectra of both types of TMSO complexes are quite similar. This similarity in the S–O vibrational region indicates that the sulfoxide is not acting as a bridging ligand in the $CuX_2 \cdot TMSO$ complex.

The complexes $3CuX_2 \cdot 4TMSO$ are probably best formulated as $[Cu(TMSO)_4][Cu_2Cl_6]$ since TMSO is not removed at 80° under high vacuum, whereas the $CuX_2 \cdot TMSO$ complexes are probably dimers with a symmetrical $\mathrm{Cu}<^{\mathrm{Cl}}_{\mathrm{Cl}}>\mathrm{Cu}$ bridge. The latter formulation is analogous to the structure[9] of $Cu_2Cl_4(CH_3CN)_2$, which exhibits the halo-bridging linkage, and the organic molecules are bonded to the copper atoms in positions which are *trans* for the entire molecule. However, the TMSO complexes do not exhibit the unusual magnetic properties of the $LiCuCl_3 \cdot 2H_2O$,[10] but are similar to those of $CsCuCl_3$.[11] Both $3CuCl_2 \cdot 4TMSO$ and $CuCl_2 \cdot TMSO$ exhibited normal magnetic behavior over the temperature range studied (Table II).

The interesting deoxygenation of the sulfoxide in the sulfur-bonded Pd(II) complex is currently under investigation.

---

[8] D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

[9] R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

[10] P. H. Vossos, L. D. Jennings, and R. E. Rundle, *ibid.*, **32**, 1590 (1960); P. H. Vossos, D. R. Fitzwater, and R. E. Rundle, *Acta Cryst.*, **16**, 1037 (1963).

[11] B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

CONTRIBUTION NO. 1238 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA

Formation of $B_{10}H_{15}^-$ as an Intermediate in Borohydride Attack on Decaborane-14[1]

BY RILEY SCHAEFFER AND FRED TEBBE

Received February 21, 1964

The reaction of decaborane-14 with borohydride salts has been studied by at least two groups of workers[2,3] and has been shown to proceed by the over-all reaction (in the case of the sodium salt)

$$2NaBH_4 + 2B_{10}H_{14} \rightarrow 2NaB_{10}H_{13} + 2H_2 + B_2H_6 \quad (1)$$

Aftandilian, *et al.*, have confirmed this observation and shown that at higher temperatures further reaction occurs to produce $B_{11}H_{14}^-$ salts,[4] and in aqueous solution, Muetterties has shown that $B_{10}H_{14}^{-2}$ salts are the principal products.[5] By monitoring the reaction with ^{11}B n.m.r. spectra at invervals we have now been able to demonstrate that in ethereal solvents the reaction largely proceeds in two stages with preliminary hydride transfer to form $B_{10}H_{15}^-$ salts and subsequent hydrogen elimination to form the previously observed $B_{10}H_{13}^-$ derivatives.

---

[1] Studies of Boranes. XIII. For part XII see R. Schaeffer and F. Tebbe, *Inorg. Chem.*, **3**, 904 (1964). Correspondence regarding this paper should be addressed to R. Schaeffer.

[2] G. W. Schaeffer, unpublished work, 1959 and earlier.

[3] W. V. Hough and L. J. Edwards, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961 p. 192.

[4] V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

[5] E. L. Muetterties, *ibid.*, **2**, 647 (1963).