CONTRIBUTION FROM PARSONS CHEMICAL LABORATORIES,
UNIVERSITY OF NEW HAMPSHIRE,
DURHAM, NEW HAMPSHIRE 03824

Complexes of Sulfoxides. III. Complexes of Dibenzyl Sulfoxide and Mixed Complexes of Dibenzyl Sulfoxide and Acetone with Divalent Ions of the First Transition Series[1]

BY JAMES H. WEBER

Received June 19, 1969

Synthetic interest in complexes of dibenzyl sulfoxide ($(bz)_2SO$) arose when it was observed that they could not be prepared by the usual synthetic routes used for other sulfoxide complexes of divalent metals of the first transition series.[2] Complexes of weak, neutral ligands are commonly prepared by dehydrating the hydrated metal perchlorates *in situ* with 2,2-dimethoxypropane[2] or better with triethyl orthoformate.[3] In neither case can $[M((bz)_2SO)_6](ClO_4)_2$ with metals of the first transition series be isolated. When either of the two dehydrating agents is used, a by-product of the dehydration reaction, acetone or an alcohol, is strongly complexed to the metal ion. For this reason the bulky solvent *t*-butyl alcohol in the absence of any dehydrating agent was used for the synthesis of the 6:1 complexes.

Experimental Section

The colors, melting points, elemental analyses, and magnetic moments of all complexes are listed in Table I.

Chemicals.—Hydrated metal perchlorates obtained from G. Frederick Smith, Columbus, Ohio, were used as received. Dibenzyl sulfoxide, obtained from Aldrich Chemical Co., was recrystallized from 50% (v/v) aqueous ethanol.

Synthetic Method A.—The $[M((bz)_2SO)_6](ClO_4)_2$ series was prepared as follows (M = Mn(II), Fe(II), Co(II), Ni(II), and Zn(II)). To a solution of 1.38 g of dibenzyl sulfoxide (6.0 mmol) in 75 ml of warm *t*-butyl alcohol was added a solution of $M(ClO_4)_2 \cdot 6H_2O$ (0.9 mmol) in 25 ml of warm *t*-butyl alcohol. The solution was stirred 5 min and allowed to cool to room temperature. The solid was filtered, washed with anhydrous ether, and dried *in vacuo* over magnesium perchlorate for 15 hr. The typical field was 60–80%. $[Cu((bz)_2SO_4](ClO_4)_2$ was prepared similarly using the appropriate stoichiometry and was recrystallized from *t*-butyl alcohol.

Synthetic Method B.—The $[M((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$ series was prepared as follows (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)). A solution of 0.92 g of dibenzyl sulfoxide (4.0 mmol) dissolved in 30 ml of hot acetone was added to a solution of $M(ClO_4)_2 \cdot 6H_2O$ (1.0 mmol) dissolved in 10 ml of hot acetone. The solution was stirred 10 min, allowed to cool to room temperature, and refrigerated for 15 hr. After filtering, the resulting solid was dried *in vacuo* over magnesium perchlorate for 15 hr. The copper(II) synthesis varied slightly from this procedure; 0.94 g of 2,2-dimethoxypropane (9.0 mmol) was stirred with the acetone solution of $Cu(ClO_4)_2 \cdot 6H_2O$ for 10 min before the ligand solution was added, and the sample was air dried after the filtration. The yields for this series were 70–85%.

Alternative Preparations of $[Cu((bz)_2SO)_4](ClO_4)_2$.—This complex was prepared by three different methods. It was prepared directly by synthetic method A and was prepared in two ways from $[Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$. In the first alternative method the acetone adduct was stirred in boiling *t*-butyl alcohol for 10 min, while the pale green adduct effervesced into the pale blue 4:1 complex. The sample was filtered and dried 15 hr *in vacuo*. In the second method a sample of $[Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$ was heated *in vacuo*. The sample contained some acetone after heating 48 hr at 60°, but it was removed by 6 hr of additional heating at 85°. The heating was done in a metal desiccator behind a safety shield because of the potential explosive nature of the complexes. The resulting gray-green product when recrystallized from *t*-butyl alcohol, gave the pale blue 4:1 complex. It was originally thought that the gray-green and blue compounds were different despite identical melting points and similar analyses, but powder patterns show that the compounds from all three procedures are identical within the sensitivity of the method.

Melting Point Determination.—Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared Measurements.—All measurements were made on a Beckman IR-12 infrared spectrophotometer using previously described techniques.[1]

Magnetic Susceptibility Measurements.—All measurements were done by the Gouy method at room temperature using previously described techniques.[2]

Analyses.—Sulfur analyses were performed by Galbraith Microchemical Laboratories. Carbon and hydrogen analyses were done at the University of New Hampshire on an F & M Model 185 analyzer. Metal analyses were done by EDTA titrations using standard techniques.[4]

Results and Discussion

The magnetic moments of the dibenzyl sulfoxide complexes in Table I are in the expected range[5] for high-spin octahedral complexes of manganese(II), iron(II), cobalt(II), and nickel(II). There is no significant difference between the values of the same metal ion in the $M((bz)_2SO)_6^{2+}$ and $M((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ series. This similarity and infrared evidence (see below) demonstrate that the acetone is coordinated in all acetone-containing complexes. The magnetic moments of $Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ and the sample of $Cu((bz)_2SO)_4^{2+}$ prepared by boiling the adduct in *t*-butyl alcohol are 2.06 and 2.04 BM, respectively. The other two methods of preparation yield 4:1 copper(II) complexes, which possess magnetic-field-dependent magnetic moments even after repeated recrystallization. The values for the gray-green sample obtained by heating *in vacuo* the acetone adduct and the directly prepared complex (method A) are 2.7 ± 0.1 BM (5.8 kG), 2.5 ± 0.1 BM (8.6 kG), and 2.4 ± 0.1 BM (11.3 kG). Attribution of this behavior to a ferromagnetic impurity seems inadequate when considering that the gray-green sample was prepared *in vacuo* from the typically paramagnetic acetone adduct. Enhanced magnetic moments for copper(II) complexes are rare but have been observed.[6,7]

(1) Part II: C. V. Berney and J. H. Weber, *Inorg. Chem.*, **7**, 283 (1968).
(2) W. F. Currier and J. H. Weber, *ibid.*, **6**, 1539 (1967).
(3) P. W. N. M. Van Leeuwen and W. L. Groeneveld, *Inorg. Nucl. Chem. Letters*, **3**, 145 (1967).
(4) (a) H. A. Flaschka, "EDTA Titrations," 2nd ed, Pergamon Press, New York, N. Y., 1964; (b) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., Princeton, N. J., 1958.
(5) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966, p 278 ff.
(6) E. Sinn, *Inorg. Nucl. Chem. Letters*, **5**, 193 (1969).
(7) J. H. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965).

TABLE I
CHARACTERIZATION OF DIBENZYL SULFOXIDE COMPLEXES[a]

Compound	Color	Mp,[b] °C	Analyses, % Calcd C	H	S	M	Found C	H	S	M	Magnetic moment,[d] BM
$[Mn(bz)_2SO)_6](ClO_4)_2$	White	157–158	61.67	5.17	11.76	3.36	61.60	5.13	11.84	3.33	6.00
$[Fe(bz)_2SO)_6](ClO_4)_2$	Pale yellow	145 dec	61.64	5.17	11.75	3.41	61.94	5.11	11.36	3.58	5.58
$[Co(bz)_2SO)_6](ClO_4)_2$	Pink	167–168	61.52	5.16	11.73	3.59	61.38	4.10	11.83	3.29	5.18
$[Ni(bz)_2SO)_6](ClO_4)_2$	Pale yellow	174–175	61.52	5.16	11.73	3.58	61.52	5.19	11.78	3.52	3.46
$[Zn(bz)_2SO)_6](ClO_4)_2$	White	139–141	61.30	5.14	11.69	3.98	61.34	5.12	11.79	3.82	
$[Mn(bz)_2SO_4A_2](ClO_4)_2$	White	139–145 dec	57.68	5.29	9.94	4.25	57.76	5.36	9.74	4.33	6.02
$[Fe(bz)_2SO_4)A_2](ClO_4)_2$	Yellow	133–134 dec	57.64	5.29	9.93	4.34	57.76	5.41	9.75	4.59	5.48
$[Co((bz)_2SO)_4A_2](ClO_4)_2$	Pink	136–137 dec	57.50	5.29	9.91	4.55	57.76	5.32	9.84	4.41	5.11
$[Ni((bz)_2SO_4)A_2](ClO_4)_2$	Pale yellow	147–150 dec	57.50	5.29	9.91	4.53	57.58	5.28	9.79	4.53	3.38
$[Cu((bz)_2SO)_4A_2](ClO_4)_2$	Pale green	189–190 dec[c]	57.28	5.27	9.86	4.88	57.22	5.42	9.96	4.81	2.06
$[Zn((bz)_2SO)_4A_2](ClO_4)_2$	White	123–129 dec	57.20	5.26	9.85	5.02	57.32	5.20	9.37	5.02	
$[Cu((bz)_2SO)_4](ClO_4)_2$	Pale blue	191–192 dec	56.81	4.76	10.83	5.36	57.76	4.67	10.51	5.11	2.04[e]

[a] Abbreviations: dec, decompose; M, metal; A, acetone; $(bz)_2SO$, dibenzyl sulfoxide. [b] Uncorrected. [c] Color change from pale green to pale blue during heating. [d] Average value at 5.8 and 8.6 kG. [e] Sample prepared by boiling the acetone adduct in *t*-butyl alcohol (see Experimental Section).

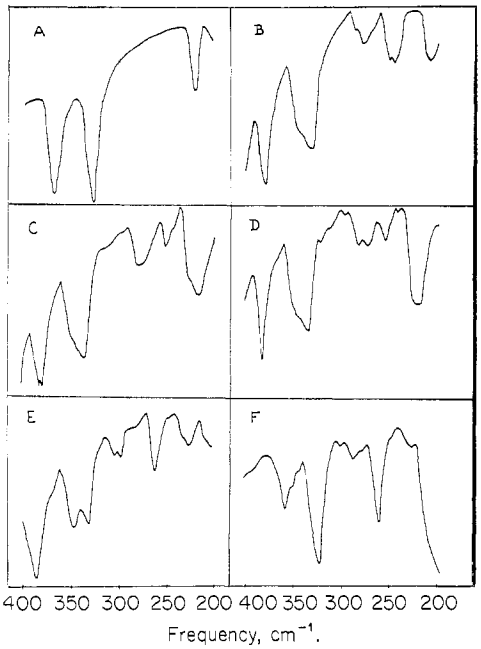

Figure 1.—Infrared spectra of dibenzyl sulfoxide ($(bz)_2SO$) and some of its complexes in the 400–200-cm^{-1} region: (A) $(bz)_2SO$; (B) $[Zn((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$; (C) $[Co((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$; (D) $[Ni((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$; (E) $[Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2](ClO_4)_2$; (F) $[Cu((bz)_2SO)_4](ClO_4)_2$.

TABLE II
SELECTED INFRARED FREQUENCIES (cm^{-1}) FOR DIBENZYL SULFOXIDE, ACETONE, AND THEIR COMPLEXES IN THE ν_{S-O} AND ν_{C-O} REGIONS[a–c]

Species	ν_{S-O}	$\Delta\nu_{S-O}$[d]	ν_{C-O}	$\Delta\nu_{C-O}$
Acetone (A)			1720 s	
$(bz)_2SO$ (L)	1032 s			
MnL_6^{2+}	970 s, 986 s	54		
FeL_6^{2+}	963 s, 978 s	62		
CoL_6^{2-}	962 s, 973 s	64		
NiL_6^{2+}	961 s, 974 s	64		
ZnL_6^{2+}	967 s, 981 s	58		
CuL_4^{2+}	(951), 957 s, (967)	74		
$MnL_4A_2^{2+}$	976 s, 987 s	50	1683 s	37
$FeL_4A_2^{2+}$	(969, 973 s	61	1682 s	38
$CoL_4A_2^{2+}$	968 s	64	1680 s	40
$NiL_4A_2^{2+}$	964 s, 972 s	64	1680 s	40
$ZnL_4A_2^{2+}$	967 s, 972 s	62	1683 s	37
$CuL_4A_2^{2+}$	948 s, 956 s	80	1694 s	26

[a] Abbreviations: $(bz)_2SO$, dibenzyl sulfoxide; s, strong; $\Delta\nu_{X-O}$, ν_{X-O}(ligand) − ν_{X-O}(complex); parentheses signify a shoulder. [b] ClO_4^- is the anion in all cases. [c] Nujol mulls. [d] From average of complex ν_{S-O}.

Selected high-frequency infrared data (Table II) show that for each complex in agreement with the expected metal–oxygen bond, the ν_{S-O} frequency decreases upon complex formation. It is well known that bond energies[8] in a series of first transition series metal complexes, *e.g.*, $M(NH_3)_6^{2+}$, increase in the order: Ni(II) > Co(II) > Fe(II) > Mn(II). Using $\Delta\nu_{SO}$ as an estimate of the relative metal–oxygen bond strength, the order of the 6:1 complexes is Ni(II) ~ Co(II) > Fe(II) > Mn(II). The order is identical with that found for ν_{M-O} of octahedral dimethyl sulfoxide[1] complexes and for $\Delta\nu_{S-O}$[9] and ν_{M-O}[10] of 6:1 tetramethylene sulfoxide complexes. From the abundance of data it is seen that $\Delta\nu_{S-O}$ and more appropriately ν_{M-O} yield relative bond strengths in closely controlled sulfoxide systems.

In the $M((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ series $\Delta\nu_{S-O}$ is not significantly different from that of the corresponding 6:1 dibenzyl sulfoxide complexes. This suggests that the four sulfoxide ligands in the acetone adducts are not very differently bonded from the way they are in the 6:1 complexes. The larger $\Delta\nu_{S-O}$ values of $Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ compared to other metal complexes of that stoichiometry are probably due to decreased steric crowding. It is seen from molecular models that dibenzyl sulfoxide has a large steric requirement and that four of the ligands can bond more tightly in the absence of two additional ligands. The $\Delta\nu_{S-O}$ difference between the copper complex and other acetone-

(8) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 77 ff.

(9) P. W. N. M. Van Leeuwen and W. L. Groeneveld, *Rec. Trav. Chim.*, **86**, 721 (1967).

(10) J. Reedijk, P. W. N. M. Van Leeuwen, and W. L. Groeneveld, *ibid.*, **87**, 1073 (1968).

TABLE III
SELECTED INFRARED FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR DIBENZYL SULFOXIDE, ACETONE (A), $M((bz)_2SO)_4A_2^{2+}$, AND $Cu((bz)_2SO)_4^{2+}$ [a-c]

$(bz)_2SO$ (L)	Acetone (A)	$MnL_4A_2^{2+}$	$FeL_4A_2^{2+}$	$CoL_4A_2^{2+}$	$NiL_4A_2^{2+}$	$ZnL_4A_2^{2+}$	$CuL_4A_2^{2+}$	CuL_4^{2+}	Assignments
	530 s[d]	556 s	556 s	558 s	556 m	557 m	562 m		δco(acetone)
		535 s	533 s	540 m	544 m	537 m	535 s		
473 s		476 s	477 s	474 s	476 s	478 s	483 s	487 s	δcso($(bz)_2SO$)
		(465)	(468)	468 m	(468)	(468)	(471)	(470)	
	385 w[d]	381 s	383 s	385 s	384 s	383 s	388 s		δccc(acetone)
372 m								360 m	
(360)									
331 m		(347)	348 m	(349)			347 m	(353)	δcso($(bz)_2SO$)
			340 m	(344)	(343)	(346)		(348)	
		339 s	334 m	340 s	338 s	335 s	334 m	324 s	
							305 w		
							301 w		
			(283)		285 w	(287)		289 w	
		277 m, br	278 w	281 m, br	276 w	280 m			
						(273)			
			(250)		257 w	253 m			
		245 m	245 w	249 m		248 m			
		~200 s	211 s	219 m	226 s, br	209 m	263 s	265 m	ν_{M-O}

[a] Abbreviations: L and $(bz)_2SO$, dibenzyl sulfoxide; A, acetone; s, strong; m, medium; w, weak; br, broad; parentheses signify a shoulder. [b] Nujol mulls. [c] ClO_4^- is the anion in all cases. [d] Reference 13.

containing complexes is undoubtedly due to a static Jahn–Teller distortion, as evidenced by the low 26-cm^{-1} $\Delta\nu_{C-O}$ value in $Cu((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$. In this complex the weakly held axial acetone allows stronger in-plane bonding than in the other acetone-containing complexes. Similar behavior is observed for $Cu((C_6H_5)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ and $Cu((C_6H_5)_2SO)_6^{2+}$, where the ligand is diphenyl sulfoxide.[11]

The dibenzyl sulfoxide infrared assignments in Table II are based on Green's study[12] of diphenyl sulfoxide to which he assigned CSO bending fundamentals at 481 and 303 cm^{-1}. By analogy the 473- and 331-cm^{-1} bands in dibenzyl sulfoxide and the bands in the complexes in the same region are also assigned to the CSO deformations. As in $Cd((C_6H_5)_2SO)_2I_2$ studied by Green, the frequency of both deformations increases upon complex formation. The CO bending fundamental in acetone[13] occurs at 530 cm^{-1}, but in the complexes this mode results in strong higher frequency bands near 558 and 540 cm^{-1}. The weak CCC deformation at 385 cm^{-1} is assigned to the strong band near 384 cm^{-1} in the complexes. A third acetone fundamental, the weak out-of-plane skeletal vibration at 484 cm^{-1}, is not observed in the complexes owing to the predominant δ_{CSO} near 478 cm^{-1}.

The assignment of ν_{M-O} in the dibenzyl sulfoxide series is difficult because of the large number of aromatic vibrations below 600 cm^{-1} (Figure 1). Several relationships may be considered in the attempt to assign ν_{M-O} in the dibenzyl sulfoxide complexes. (1) As the mass of the ligand increases, ν_{M-O} decreases. Thus ν_{M-O} should be lower than the 325-cm^{-1} frequency found in analogous pyridine N-oxide complexes.[14] (2) The usual metal order of frequency, Ni(II) > Co(II) > Fe(II) > Mn(II), should be observed. (3) As the coordination number of the complex with the same ligand decreases, ν_{M-O} increases. For example, ν_{M-O} for CuL_4^{2+} is about 50 cm^{-1} higher than that for the NiL_6^{2+} analog when L is tetramethylene sulfoxide[10] or dimethyl sulfoxide.[1,15] The series of bands (Figure 1, Table III) which best fulfills the criteria is found in the $M((bz)_2SO)_4(CH_3C(O)CH_3)_2^{2+}$ series at 263 cm^{-1} for Cu(II) and near 220 cm^{-1} for other M(II), and in $Cu((bz)_2SO)_4^{2+}$ at 265 cm^{-1}.

Acknowledgment.—The preparation of Figure 1 by Anne C. Weber is appreciated. This research was supported in part by the Central University Research Fund, Grant No. 358.

(11) P. W. N. M. Van Leeuwen, *Rec. Trav. Chim.*, **86**, 201 (1967).
(12) J. H. S. Green, *Spectrochim. Acta*, **24A**, 1627 (1968).
(13) G. Dellepiane and J. Overend, *ibid.*, **22**, 593 (1966).
(14) Y. Kakiuti, S. Kida, and J. V. Quagliano, *ibid.*, **19**, 201 (1963).
(15) J. H. Weber, *Inorg. Nucl. Chem. Letters*, in press.

CONTRIBUTION NO. 2423 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Protonation of Carbonyl Groups in Aminocarboxylate Coordination Compounds

BY JAMES L. SUDMEIER, KENNETH E. SCHWARTZ, AND ALAN J. SENZEL

Received June 19, 1969

There has been considerable study[1] of protonation of carbonyl groups in aliphatic ketones, aldehydes, carboxylic acids, esters, anhydrides, and simple amides. Recently we reported on the protonation of carbonyl groups in peptides and amino acids.[2] Now we wish to report that carbonyl groups in certain aminocarboxylate coordination compounds are protonated in FSO_3H–

(1) See references quoted in ref 2.
(2) J. L. Sudmeier and K. E. Schwartz, *Chem. Commun.*, 1646 (1968).