reaction, by analogy to the formation of $MoS_nO_{4-n}$ species is very likely

$$MoS_4^{2-} + H_2O \rightarrow MoS_3O^{2-} + H_2S$$

followed by reaction of the intermediate

$$MoS_3O^{2-} + MoS_4^{2-} + {}^1/_2O_2 + H^+ \rightarrow Mo_2S_7O^{2-} + OH^-$$

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**Registry No.** $[(n\text{-}Bu)_4N]_2[Mo_2S_7O]$, 97689-85-5; $(NH_4)_2MoS_4$, 15060-55-6.

**Supplementary Material Available:** Listings of bond distances and angles of the cation, anisotropic thermal parameters, hydrogen atom parameters, and structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

# Notes

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## Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 7.[1] Bis[μ-2-(diethylamino)ethanolato]dibromodicopper(II)

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In this series of papers the **g** and **D** tensors of dinuclear copper(II) complexes were measured, showing that in any case a dominant contribution[1,3-8] of the exchange interaction to the zero field splitting was operative. For all the studied complexes in which the bridging ligands were oxygen atoms, either hydroxo or alkoxo in nature, the coordination environment around the copper ions was tetragonally distorted with the bridging ligands occupying two adjacent equatorial positions. The value of $D$ was found to be uncorrelated to the isotropic exchange constant, $J$, but a smooth tendency to a decrease in $D_{zz}$ as the copper-copper, $r$, distance increases was evident.[3]

Recently the crystal structure[9,10] and the temperature dependence of the magnetic susceptibility[11] of bis[μ-2-(diethylamino)ethanolato]dibromodicopper(II) was reported. The complex is dinuclear with each copper ion coordinated to a bromine, to a nitrogen atom of the aminoalcohol, and to the two bridging oxygen atoms. The coordination environment is close to square planar, with a significant tetrahedral distortion. The magnetic susceptibility data showed that the two metal ions are coupled in an antiferromagnetic way, with a singlet-triplet splitting of 817 $cm^{-1}$.

Since the reported copper-copper distance,[9] 3.033 (5) Å, falls in a region of our $D_{zz}$ vs. $r$ plot where only one data point is available,[3] we decided to measure the single-crystal EPR spectra of the compound, in order to obtain $D_{zz}$ and see if it confirms the relation with the copper-copper distance.

Single crystals of the compound prepared as previously described[9] were grown by slow evaporation of ethanol solutions. They have a complex shape with $(10\bar{1})$ and $(\bar{1}01)$ best developed faces. Polycrystalline powder EPR spectra, recorded at room temperature at the Q-band frequency, are shown in Figure 1. They are similar to those of the other members of the series, being broad and showing no resolved copper hyperfine splitting. Single-crystal EPR spectra were recorded at the Q-band frequency by rotating, with a one-circle goniometer, around $b$, the $y$ laboratory axis, $x$, which is orthogonal to $b$ in the (101) face, and $z = x \times y$. An analysis of the data, performed with the procedure previously described,[4] yielded the **g** and **D** tensors. They are shown in Table I, the principal directions being expressed as direction cosines referred to the laboratory frame. As in the other members of the series, the largest $D$ component, $D_{zz} = -0.372$ (7) $cm^{-1}$, is found roughly parallel to the direction of the largest $g$ value, while the smallest $D$ component, $D_{xx} = 0.140$ (6) $cm^{-1}$, is found parallel to the copper-copper direction. The negative sign of $D_{zz}$ is assigned on the basis of considerations developed elsewhere.[3]

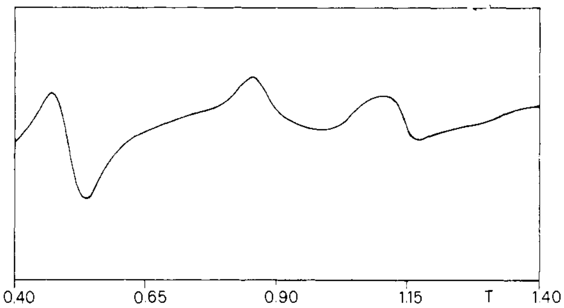

**Figure 1.** Polycrystalline powder EPR spectrum at the Q-band frequency and room temperature of bis(μ-(2-diethylamino)ethanolato)dibromodicopper(II).

**Table I.** Principal Values and Directions of **g** and **D** Tensors[a] for Bis[μ-2-(diethylamino)ethanolato]dibromodicopper(II)

| $g_{xx}$ | $g_{yy}$ | $g_{zz}$ |
|---|---|---|
| 2.08 (1) | 1.98 (2) | 2.19 (2) |
| 0.7 (1) | −0.58 (8) | 0.4 (1) |
| −0.07 (9) | 0.51 (5) | 0.86 (2) |
| −0.7 (1) | −0.63 (8) | 0.3 (1) |
| $D_{xx}$[b] | $D_{yy}$[b] | $D_{zz}$[b] |
| 0.140 (6) | 0.231 (8) | −0.372 (7) |
| 0.46 (4) | −0.73 (2) | 0.499 (9) |
| 0.27 (4) | 0.65 (1) | 0.708 (5) |
| −0.84 (1) | −0.19 (5) | 0.500 (8) |

[a] The directions are given by the cosines referred to the laboratory frame specified in the text. [b] In $cm^{-1}$.

The **g** tensor is determined only with moderate accuracy, and experimental errors must be the explanation for the low value of $g_y = 1.98$ (2).

The observed $|D_{zz}|$ value is smaller than that previously reported[3] for bis(μ-hydroxo)bis[bis(2-methylimidazole)copper(II)] diperchlorate dihydrate, in which the copper-copper distance is 2.993

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(1) Part 6: Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1985**, *24*, 704.

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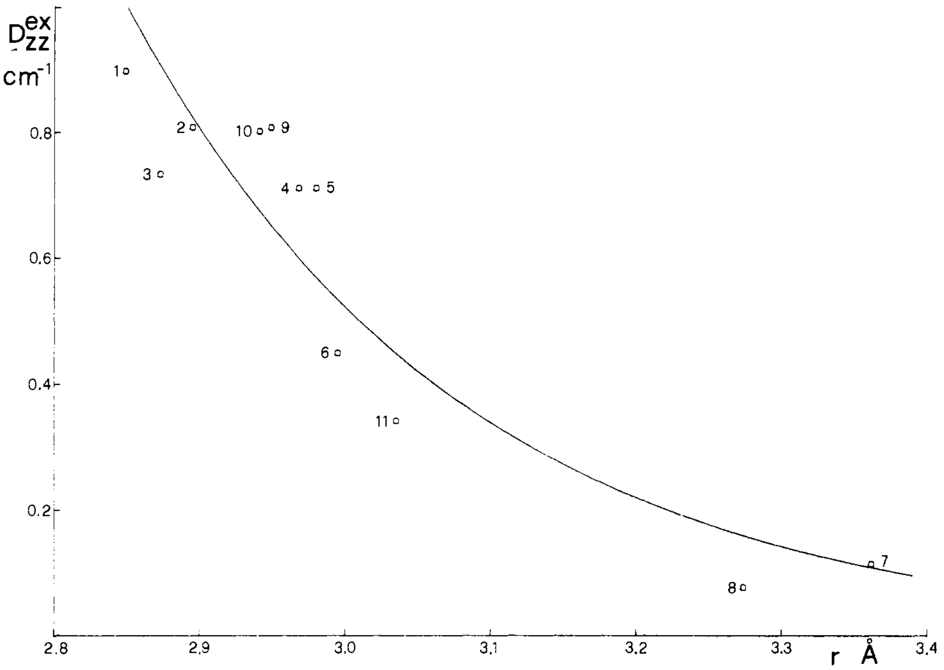

**Figure 2.** $D_{zz}$ exchange values vs. copper–copper distance with the calculated curve for exponential regression for the following compounds: (1) bis($\mu$-hydroxo)bis[(bipyridyl)copper(II)] dinitrate;[15] (2) bis($\mu$-hydroxo)bis[(bipyridyl)copper(II)] sulfatepentahydrate;[4,5,16] (3) bis($\mu$-hydroxo)bis[(bipyridyl)copper(II)] diperchlorate;[17] (4) bis($\mu$-hydroxo)bis[(*N,N,N′,N′*-tetramethylethylenediamine)copper(II)] diperchlorate;[18] (5) bis($\mu$-hydroxo)bis[(*N,N,N′,N′*-tetraethylethylenediamine)copper(II)] diperchlorate;[19] (6) bis($\mu$-hydroxo)bis[bis(2-methylimidazole)copper(II)] diperchlorate dihydrate;[3] (7) bis($\mu$-pyridine *N*-oxide)bis[(pyridine *N*-oxide)dichlorocopper(II)];[20,21] (8) bis($\mu$-pyridine *N*-oxide)bis[dichloroaquocopper(II)];[21-23] (9) dipiperidinium bis[($\mu$-methoxo)bis(2,4-dinitrophenolato)cuprate(II)]-2-methanol;[24] (10) dipiperidinium bis[($\mu$-methoxo)bis(2,4-dinitrophenolato)cuprate(II)];[24] (11) bis[$\mu$-2-(diethylamino)ethanolato]dibromodicopper(II).

Å, thus confirming the tendency to a decrease of the zero-field splitting on increasing *r*. Since eleven experimental points are now available for dinuclear copper(II) complexes bridged by two oxygen donors, we tried to fit the data to a curve. The simplest possible regression functions are linear of course. The data are fit to $D_{zz} = a + br$, with $a$ = 5.3099 (0.0314) cm$^{-1}$ and $b$ = −1.5685 (0.0099) cm$^{-1}$ Å$^{-1}$. The $R^2$ linear correlation coefficient is 0.8776, and the variance is 0.0019 cm$^{-1}$.

Another possibility is that of fitting the data to an exponential curve, $D_{zz} = a \exp(br)$, or to a power curve $D_{zz} = ar^b$, since some suggestions have been made in the literature for such dependencies of the exchange interactions.[12-14] In Figure 2 we report the results of the fit to an exponential curve corrected by subtracting the calculated dipolar component from the experimental values. The results for the $D_{zz} = ar^b$ curve are practically identical. The quality of the fit is comparable to that of the linear regression. The main deviation of the linear and the exponential curves is for long copper–copper distances, since the linear regression predicts a change in sign of $D_{zz}$, while the exponential curve demands that the exchange contribution goes to zero for long distances. Of course the latter alternative seems more reasonable.

The results of the present analysis must be interpreted in the sense that they show that a relation between $D_{zz}$ and *r* does exist, although it cannot be satisfactorily expressed with a simple curve, since several factors that are expected to affect the exchange contribution to **D**, such as the nature of the bridging oxygen, the metal–oxygen distance, and the detailed coordination geometry around the copper ions, cannot be considered as constant throughout the series. It is hoped however that the reported curves can be useful as a first guess of the copper–copper distance in a complex of unknown structure, once **D** is experimentally determined.

**Registry No.** Bis($\mu$-2-(diethylamino)ethanolato)dibromodicopper(II), 75583-54-9.

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## $[Mo_3(\mu_3\text{-}O)_2(O_2CC_6H_5)_6(H_2O)_3](ClO_4)_2 \cdot HClO_4 \cdot 3CH_3CH_2OH$: Corrigendum

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*Received January 18, 1985*

The crystal structure of this compound[1] was reported as triclinic, space group $P\bar{1}$, with $a$ = 13.837 (3) Å, $b$ = 22.189 (5) Å, $c$ = 11.394 (3) Å, $\alpha$ = 92.39 (1)°, $\beta$ = 114.35 (1)°, $\gamma$ = 89.02 (1)°, and $Z$ = 2. It is correctly described as monoclinic, space group $C2/c$. The vectors (001), (201), and (010) describe a cell with $a'$ = 11.394 Å, $b'$ = 25.212 Å, $c'$ = 22.189 Å, $\alpha'$ = 90.00°, $\beta'$ =

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