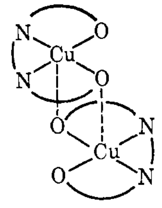
Correspondence

Spin–Spin Coupling in Parallel Planar Copper(II) Dimers

Sir:

In a recent correspondence Sinn[1] noted that there were no precedents for significant coupling of the spins of the copper(II) ions in dimers such as *N,N'*-ethylenebis(salicylaldiminato)copper(II)[2] (I). In the last few months we[3–22] have determined the properties of several copper(II) compounds with structural features similar to I and believe that it is appropriate to present an assessment of our observations since the results have a direct bearing on this important point.


I

The experimental approach which has been taken consists of electron paramagnetic resonance studies and low-temperature magnetic susceptibility determinations on compounds which are known from X-ray studies to have structures which may be generally described as parallel planar monomeric units linked by relatively long out-of-plane bonds. The magnetic and structural data for several of these compounds are collected in Table I. In addition to data for dimers with oxygen bridging atoms, data are also presented for two compounds with chloride bridges and two compounds with sulfur bridges. Since the number of copper dimers with parallel planar structures and bridges other than oxygen is limited, data have been included for $Cu_2Cl_8^{4-}$ and Cu(ddts) although, strictly speaking, neither belongs to the structural class. The $Cu_2Cl_8^{4-}$ ion is considered to be distorted trigonal bipyramids sharing base-to-apex edges,[4,16] and Cu(ddts) has a chain structure with alternating long and short Cu–S out-of-plane bonds.[23]

TABLE I

MAGNETIC AND STRUCTURAL PARAMETERS FOR COPPER DIMERS

Cluster	Bridge	2*J*, cm⁻¹	Cu–X–Cu, deg	Cu–Cu, Å	Cu–X, Å	Ref
$Cu_2Cl_8^{4-}$	Cl^-	−8.5	95[j]	3.7	2.3–2.7	4, 8, 16
$[Cu(\alpha\text{-pic})_2Cl_2]_2$[a]	Cl^-	−4	101[k]	>4	2.3–3.4	13
$[Cu(ddts)]_2$[b]	S	−14	~90[l]	3.8	2.3–3.1	7
$[Cu(edtc)_2]_2$[c]	S	+12	~90[m]	...	2.3–2.85	10, 11, 15
$[Cu(pyNO)_2(NO_3)_2]_2$[d]	O	+10	103[n]	3.5	2.0–2.4	6
$[Cu(8\text{-}OQuin)_2]_2$[e]	O	−1	...	...	2.0–2.8[o]	17
$[Cu(SALen)]_2$[f]	O	+18	89[p]	3.2	2.0–2.4	5, 18
$[Cu(CH_3SAL)_2]_2$[g]	O	+8	80[q]	3.2	1.9–2.4	19
$[Cu(dmg)_2]_2$[h]	O	+40	...	...	1.9–2.4[r]	3, 9, 22b
$[Cu(dl\text{-}tartrate)]_2^{4+}$		−18	...[s]	3.05	1.95	20
$[Cu(tyr)_2]_2$[i]	O	+20	...	...	2.0–2.4[t]	22

[a] α-pic = α-picoline. [b] ddts = diacetylbis(thiosemicarbazone). [c] edtc = diethyldithiocarbamato ion. [d] pyNO = pyridine *N*-oxide. [e] 8-OQuin = 8-hydroxyquinolate ion. [f] SALen = *N,N'*-ethylenebis(salicylaldiminate) ion. [g] *N*-Methylsalicylaldiminate ion. [h] dmg = dimethylglyoximate ion. [i] tyr = tyrosinate ion. [j] References 4 and 16. [k] V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25,** 1795 (1969). [l] Reference 23. [m] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19,** 886 (1965). [n] S. Sćavnicar and B. Matkovic, *Acta Crystallogr., Sect. B*, **25,** 2046 (1969). [o] G. Palenik, *ibid.*, **17,** 687 (1964). [p] Reference 2. [q] D. Hall, S. V. Sheat, and T. N. Waters, *J. Chem. Soc. A.*, 460 (1968). [r] E. Frasson, R. Bardi, and S. Bezzi, *Acta Crystallogr.*, **12,** 201 (1959). [s] Reference 20. [t] C. E. Tatsch and D. Van Der Helm, *Acta Crystallogr., Sect. A*, **25,** S192 (1969).

First, electron paramagnetic resonance spectra and low-temperature magnetic data have shown conclusively that the triplet state obtains in each compound in the table. Details concerning the magnetic resonance and susceptibility data have been presented elsewhere.[3–22] For those compounds with singlet ground states and negative *J* values, the evaluation of the singlet–triplet splitting is easily obtained with a great deal of precision from a least-squares fit of the magnetic susceptibility data to eq 1 resulting from substitution into the Van Vleck equation[24] where the symbols have their usual meaning and in most cases $\theta \leq 3°$.

$$\chi_m = \frac{2g^2N\beta^2}{3k(T-\theta)}\left\{1 + \frac{1}{3}\exp(-2J/kT)\right\}^{-1} + N\alpha \quad (1)$$

The constant θ allows for intermolecular interactions between dimers. However, for those compounds with triplet ground states and positive *J* values, the value for singlet–triplet splitting cannot be determined with the same degree of confidence and precision from the least-squares fit of the data to eq 1. Only a careful examination of the fitting parameters will permit an estimation of the singlet–triplet splitting.[15] For the positive *J* values discussed here, the accuracy is probably no better than ±10%, for it is usually beyond this range in *J* that the fitting parameter begins to increase significantly.

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The most obvious conclusion to be drawn from the data in Table I is simply that spin–spin coupling can exist between copper(II) ions in the structural class under discussion. It may also be important to point out that the magnitudes of the single–triplet splitting span a relatively wide range of energy, an observation which suggests that the strength of the interaction between the two copper ions may not be reflected directly by the energy-splitting alone. In speculation on this point, it may be offered that the various effects which contribute to the mechanism of the spin-coupling interaction may have different signs thus modulating the magnitude of the singlet–triplet splitting according to the relative importance of the contributing effects.

Acknowledgments.—This research has been supported by the National Science Foundation under Grant No. GP-22887 and by the Materials Research Center of the University of North Carolina through Contract SD-100 with the Advanced Research Projects Agency. We are grateful for this continuing support.

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RECEIVED FEBRUARY 19, 1971

A Modified Unterzaucher Procedure for the Determination of Total Oxygen in Organometallic Compounds

Sir:

The determination of oxygen in new research compounds has often been a missing link in the total elemental analysis of these compounds. In many instances, especially in the case of organometallic compounds, oxygen has either been determined by difference or been ignored. On the other hand, if a convenient and reliable method for the determination of oxygen were available, such an analysis would be extremely useful in helping ascertain the composition of such new compounds.

Previous methods for the determination of oxygen based on the Unterzaucher method have given perplexing, erratic results, due in part to the nonselectivity in absorbing the carbon dioxide produced.[1–4] This results in a lowering of both the sensitivity and the accuracy of the method. Several modifications of the Unterzaucher procedure have appeared.[5–7] However, none of these has dealt with the determination of oxygen in organometallic compounds.

In the past few years, several papers have appeared using the technique of neutron activation in the analysis of oxygen.[8,9] While this method does offer the possibility of determining the oxygen content of various chemical compounds including metal oxides, the overall costs and time required are such that neutron activation methods are not applicable to routine analyses.

Recently we reported our own modification of the Unterzaucher method for the determination of oxygen.[10] While this particular modification was developed for the determination of oxygen (5 ppm to several per cent) in organic compounds, we suggested the potential utility of the method to nonorganic, oxygen-containing compounds. The purpose of the present correspondence is to disclose to the practicing chemist the availability of a simple yet practical and precise method for the routine determination of oxygen in most organometallic and inorganic compounds.

The basic procedure, which has been previously described in detail,[10] involves the pyrolysis of a preweighed sample at 1050° in the presence of high purity carbon. This converts all the oxygen in the sample to carbon monoxide. The process is carried out in a stream of helium which is used to elute the pyrolysis products. These are then separated into carbon monoxide and other gases by means of a molecular sieve column in a gas chromatograph. The amount of carbon monoxide formed is determined using a thermal conductivity detector. Our procedure is applicable to the determination of oxygen not only in solids, but also liquid and gaseous compounds as well. No apparatus blank is required to obtain a useful measure of oxygen down to 10 ppm. Our method has the further advantage that very small sample sizes are required for the determination of oxygen in most compounds. In Table I, some representative sample sizes for compounds containing various percentages of oxygen are given.

TABLE I
CONVENIENT SAMPLE SIZES FOR THE DETERMINATION OF OXYGEN

% oxygen present	Sample size, mg
20–100	<0.5[a]
10–20	0.5–1.0
5–10	1.0–2.0
1–5	2.0–5.0
0–1 (trace)	5.0–30

[a] The sensitivity of the method is such that even smaller sizes are usable; however, weighing inaccuracies necessitate 0.5-mg samples.

Table II lists some typical oxygen-containing organometallic compounds which have recently been analyzed by our method, together with the calculated percentages of oxygen in each compound. These compounds contain a variety of metals, metalloids, phosphorus, halogens, etc., and are reasonably representative of the new types of organometallic compounds which are being synthesized daily in laboratories around the world.

We should point out that special consideration must be given compounds being analyzed for oxygen in the presence of fluorine by our method. A preconditioning of the pyrolysis tube is required in this instance to prevent the fluorine from reacting with

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