Proton Relaxation in Various Copper (II) Complexes and Determination of the Singlet-Triplet Separation

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Z. Naturforsch. **35 a**, 92—97 (1980); received December 3, 1979

Proton spin-lattice relaxation rates have been measured at 30 MHz as a function of temperature for a large number of dimeric copper complexes with the ligands 8-hydroxyquinoline, pyridine-N-oxide, methyl and dimethyl pyridine-N-oxide, and quinoline-N-oxide. Two carboxylates and adducts of several complexes with various solvents have also been studied. In contrast to some compounds with a normal magnetic behaviour, for most complexes a temperature dependent relaxation has been observed which agrees well with the concept of a weak antiferromagnetic interaction between the two Cu^{2+} ions. The singlet-triplet separations or exchange integrals have been determined.

I. Introduction

A large number of copper (II) compounds have been reported which possess a subnormal magnetic moment at room temperature due to electronic spin-spin coupling [1]. Most of them are dimeric complexes containing two copper (II) ions in a molecule. The best known example is perhaps copper (II) acetate monohydrate [2].

The reduced magnetic moment is the consequence of a weak antiferromagnetic interaction between the two Cu^{2+} ions within a dimeric unit giving a singlet ground state and a thermally accessible magnetic triplet state slightly above. The separation between singlet und triplet state, the exchange integral J, is the most interesting parameter when discussing magnetic properties of these compounds.

The ordinary method for determining the exchange integral is a magnetic susceptibility measurement, or, less frequently, the measurement of the electron spin resonance (ESR) intensity as a function of temperature [2, 3]. In both cases, the quantity measured is directly proportional to the population of the magnetic triplet state, c_{tr}:

$$c_{tr} = \frac{1}{1 + 1/3 \exp(-J/kT)} \,. \tag{1}$$

Recently, proton spin-lattice relaxation measurements have been successfully applied to determine the exchange integral of two dimeric complexes. Svare and Tunstall [4] studied the copper acetate complex $Cu(CH_3COO)_2 \cdot H_2O$, and Sakaguchi et al. [5] investigated a member of the numerous complexes with pyridine-N-oxide (PNO), $Cu(PNO)Cl_2 \cdot H_2O$. These authors applied an equation for the temperature dependence of the relaxation rate $1/T_1$ derived by Obata [6]:

$$\frac{1}{T_1} = K \frac{c_{tr}}{(1 - c_{tr}/3)^{1/2}} \tag{2}$$

where K is a numerical factor which can be related to the crystal structure and intermolecular interactions.

Obata's calculations, which were originally limited to the acetate complex are based on the following assumptions. The relaxation of the protons is provided by dipolar coupling with the electronic spins of the magnetic molecules. And, second, the dynamics of the electron spin system are dominated by weak intermolecular interactions between adjacent binuclear units. The most remarkable result of his calculations is the fact that Eq. (2) does not contain any electronic correlation time indicating that the frequency spectrum of electronic spin fluctuations is temperature independent in the range of the nuclear Larmor frequency.

The purpose of this paper is to show the general applicability of spin-lattice relaxation measurements and to determine exchange integrals of numerous dimeric copper complexes. A large number of complexes with the ligands 8-hydroxyquinoline (HQN), pyridine-N-oxide (PNO), quinoline-N-oxide (QNO), lutidine-N-oxide (LNO) and

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two carboxylate complexes have been studied. Some advantages of relaxation measurements as compared with the more conventional techniques are discussed.

It has to be mentioned that very recently the first direct measurement of the singlet-triplet splitting by inelastic neutron scattering was reported [7]. This technique seems to be much more accurate and trustworthy than all indirect methods. But the experimental requirements will strongly limit a general application.

II. Experimental

The organic compounds pyridine-N-oxide (PNO), 2-methylpyridine-N-oxide ($2\text{-}CH_3\text{-}PNO$), 3-methylpyridine-N-oxide ($3\text{-}CH_3\text{-}PNO$), 4-methylpyridine-N-oxide ($4\text{-}CH_3\text{-}PNO$), 4-nitropyridine-N-oxide ($4\text{-}NO_2\text{-}PNO$), quinoline-N-oxide (QNO), 2,6-lutidine-N-oxide (LNO) and 8-hydroxyquinoline (HQN) were obtained commercially and used without further purification.

The 1:1 complexes with aromatic N-oxides were prepared by mixing a solution of the ligand in ethanol with a stoichiometric amount of $CuCl_2$ or $CuBr_2$ in ethanol. The products either crystallize immediately or after standing for a short time.

The complex $Cu(2\text{-}CH_3\text{-}PNO)Cl_2$ cannot be obtained following the general procedure [8]. It was prepared by heating the methanol adduct for several hours at about 80 °C.

The adducts with dimethyl sulfoxide (DMSO) easily precipitate when the compounds are recrystallized from DMSO. In the case of the lutidine-N-oxide complexes no adduct can be obtained. The 2:1 complexes $Cu(LNO)_2Cl_2$ and $Cu(LNO)_2Br_2$, are formed instead. Starting with the complex $Cu(2\text{-}CH_3\text{-}PNO)Cl_2$ a mixture of the adduct $Cu(2\text{-}CH_3\text{-}PNO)Cl_2\cdot$ DMSO and the 2:1 compound $Cu(2\text{-}CH_3\text{-}PNO)_2Cl_2$ is obtained which can be easily distinguished because of their different colour.

The adducts with methanol can be obtained when CH_3OH is used as a solvent. Some of them are very instable and cannot be dried without decomposition. They were sealed in a glass tube immediately after filtration. The vapour pressure of the adsorbed solvent on the surface of the crystals reduces the sample decomposition. The complex $Cu(PNO)Cl_2 \cdot H_2O$ crystallizes when an aqueous solution is slowly evaporated.

Table 1. Results of elementary analyses of some complexes. Observed and calculated data are given. PNO = pyridine-N-oxide. DMSO = dimethyl sulfoxide.

Compound	C %		H %		N %	
	obs.	calc.	obs.	calc.		
$Cu(2\text{-}CH_3\text{-}PNO)Cl_2$	29,29	29,59	2,90	2,90	5,69	5,75
$Cu(PNO)Br_2\cdot$ DMSO	20,67	21,18	2,74	2,77	3,53	3,53
$Cu(4\text{-}CH_3\text{-}PNO)Cl_2$	29,49	29,86	4,01	4,04	4,42	4,35

Copper acetate monohydrate is commercially available while the corresponding succinate complex was prepared as described by Figgis and Martin [9]. The preparation of the complexes with 8-hydroxyquinoline was reported by Harris et al. [10].

Elementary microanalyses for carbon, hydrogen, and nitrogen were performed by conventional techniques for all the compounds but the instable methanol adducts. The exact content of CH_3OH is not known for the latter. Analytical data for some of the complexes which were synthesized the first time are given in Table 1.

The proton spin-lattice relaxation was measured with a Bruker pulsed spectrometer at a frequency of 30 MHz. For all measurements $90°\text{-}\tau\text{-}90°$ pulse sequences were employed. Within the temperature range 100 K to 350 K the temperature was controlled by a home-made gas-flow cryostat while a commercial continuous flow liquid helium cryostat was used for temperatures below.

III. Results

In general, the recovery of proton magnetization was found to be purely exponential within experimental error. The relaxation rate $1/T_1$ can then be determined using Eq. (3)

$$M_z(t) = M_0[1 - \exp(-t/T_1)], \tag{3}$$

where $M_z(t)$ and M_0 are the magnetization in field direction at time t and in equilibrium, respectively.

Only at lower temperatures, some compounds exhibit a non-exponential relaxation behaviour. The experimental recovery function of proton magnetization could always be fitted with satisfactory agreement using Eq. (4)

$$M_z(t) = M_0[1 - x\exp(-t/T_1') - (1-x)\exp(-t/T_1'')] \tag{4}$$

with $0 < x < 1$.

The numerical factor x simply describes the relative contribution of both exponentials to the complete recovery function. It must be emphasized that Eq. (4) is only a mathematical expression suitable to fit the experimental results. Without further justifications neither $1/T_1'$ nor $1/T_1''$ can be interpreted in terms of relaxation rates.

No attempt was undertaken to study the non-exponential behaviour in detail. $1/T_1$ values obtained from non-exponential relaxation functions were used only to support the results derived from measurements at higher temperatures with exponential recovery functions. This will be demonstrated by means of Figure 1.

Figure 1 illustrates two examples of the typical temperature dependence of the spin-lattice relaxation rate $1/T_1$ in dimeric complexes. Open symbols indicate data derived from an exponential, full symbols are from non-exponential relaxation functions. The solid line is a data fit by Equation (2). As far as a non-exponential behaviour was observed the fitting procedure was performed in two steps. First, only data of Sect. B with exponential relaxation were taken into account. The fitted dependence of $1/T_1$ was then extrapolated to lower temperatures where non-exponential behaviour occurs (Section C). Now those parameters from Eq. (4), i.e. $1/T_1'$ or $1/T_1''$, which seemed to correspond to the relaxation mechanism in section B were chosen and are shown in Figure 1. Including these additional data a final fit was made.

It is obvious that over an extended temperature range Eq. (2) describes the observed temperature dependence of the relaxation rate with excellent agreement. For the determination of the exchange integral only this temperature range is of interest.

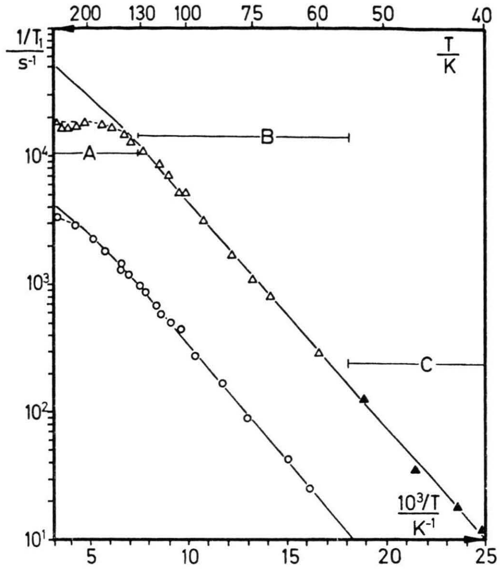

Fig. 1. The dependence of the proton spin-lattice relaxation rate $1/T_1$ upon reciprocal temperature at 30 MHz for the copper carboxylate complexes $Cu(CH_3\text{-}COO)_2 \cdot H_2O$ (△, ▲) and $Cu(COO\text{-}C_2H_4\text{-}COO) \cdot 2\,H_2O$ (○). Full symbols are data derived from non-exponential relaxation functions as discussed in the text.

At higher temperatures (Sect. A) deviations occur and the data have to be neglected for this specific problem.

In most compounds studied the splitting-energy is large and the condition $J \gg kT$ is fullfilled for the interesting temperature range. Then Eq. (2) can be simplified to give

$$1/T_1 = K' \exp(-J/kT)\,. \tag{5}$$

Thus, J can be easily determined from the slope of the linear part of a semilogarithmic plot of $1/T_1$ versus inverse temperature. In Tables 2, 3 and 4 all

Compound	J/k [K]	Literature data		
		J/k	Method	Ref.
$Cu(HQN)NO_3 \cdot H_2O$	372	455	Susceptibility	[12]
$Cu(HQN)Cl$	623	—		
$Cu(HQN)Br$	415	—		
$Cu(CH_3{-}COO)_2 \cdot H_2O$	421	411	Susceptibility	[13]
		430	Susceptibility	[14]
		370	ESR-Intensity	[2]
		446	T_1 (^1H) at 10 MHz	[4]
		429	Neutron scattering	[7]
$Cu(COO{-}CH_2{-}CH_2{-}COO) \cdot 2\,H_2O$	440	476	Susceptibility	[15]
		484	Susceptibility	[13]

Table 2. Results of singlet-triplet splitting in dimeric complexes with 8-hydroxyquinoline (HQN) and carboxylic acids. Data reported in the literature are included for comparison.

Table 3. Same as Table 2, for dimeric N-oxide complexes. PNO = pyridine-N-oxide, QNO = quinoline-N-oxide, LNO = lutidine-N-oxide. * High temperature modification.

	J/k [K]	Literature data		
		J/k	Method	Ref.
$Cu(PNO)Cl_2$	748	886	Susceptibility	[16]
		935	Susceptibility	[17]
		1030	Susceptibility	[18]
		1036	Susceptibility	[19]
$Cu(PNO)Br_2$	1343	1346	Susceptibility	[20]
$Cu(2\text{-}CH_3\text{-}PNO)Cl_2$	415	—		
$Cu(2\text{-}CH_3\text{-}PNO)Br_2$	1043	—		
$Cu(3\text{-}CH_3\text{-}PNO)Cl_2$	1043	—		
$Cu(3\text{-}CH_3\text{-}PNO)Br_2$	1243	—		
$Cu(4\text{-}CH_3\text{-}PNO)Cl_2$	1160	1193	Susceptibility	[18]
$Cu(4\text{-}CH_3\text{-}PNO)Br_2$	1000	—		
$Cu(QNO)Cl_2$	1480	—		
$Cu(QNO)Br_2$	1797	—		
$Cu(LNO)Cl_2$	1269	—		
$Cu(LNO)Br_2$	1772	—		
$Cu(4\text{-}NO_2\text{-}PNO)Cl_2$	669	761	Susceptibility	[18]
$Cu(PNO)Cl_2 \cdot H_2O$	1238	1357	Susceptibility	[3]
		1266	ESR-Intensity	[3]
		1367	ESR-Intensity	[5]
		1261	$T_1(^1H)$ at 16 MHz	[5]

splitting energies either obtained by Eq. (2) or by Eq. (5) are presented.

Equations (2) and (5), respectively, postulate a field independent relaxation rate. To verify this experimentally, additional measurements at 16 MHz and 55 MHz were performed for selected samples. Figure 2 illustrates the results. Though the absolute values of $1/T_1$ reveal a slight field dependence, the slope and consequently the value of J is invariant of the applied external field.

For comparison, the compounds $Cu(2\text{-}CH_3\text{-}PNO)_2Cl_2$, $Cu(LNO)_2Cl_2$ and $Cu(LNO)_2Br_2$ which display a normal magnetic moment [11] were investigated, too. Their relaxation rate was found to be $948 \pm 20\ sec^{-1}$, $1100 \pm 100\ sec^{-1}$ and $1300 \pm 50\ sec^{-1}$ between 300 K and 100 K, independent upon temperature. Here, the magnetic data as well as the relaxation measurements exclude an antiferromagnetic spin coupling.

Figure 3, finally, shows two examples of the temperature dependence of the relaxation rate for complexes where structural transformations occur. Therefore, for such materials Table 4 gives two

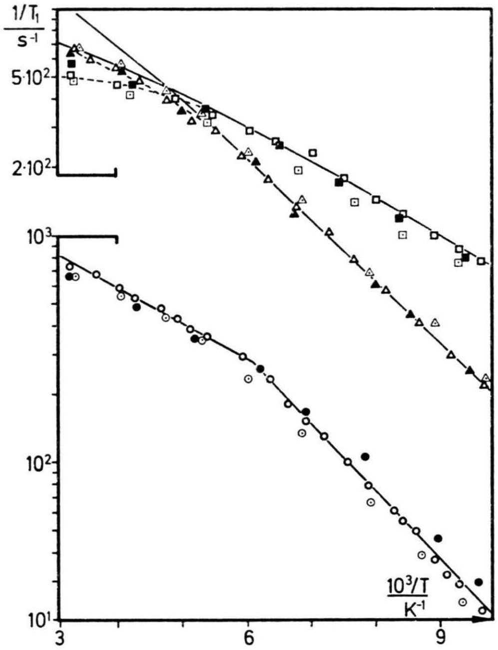

Fig. 2. The dependence of $1/T_1$ upon reciprocal temperature at 16 MHz (full symbols), 30 MHz (open symbols), and 55 MHz (⊙, ◬, ⊡) for $Cu(2\text{-}CH_3\text{-}PNO)Cl_2$ (□), $Cu(4\text{-}CH_3\text{-}PNO)Br_2 \cdot DMSO$ (△), and $Cu(PNO)Br_2 \cdot DMSO$ (○).

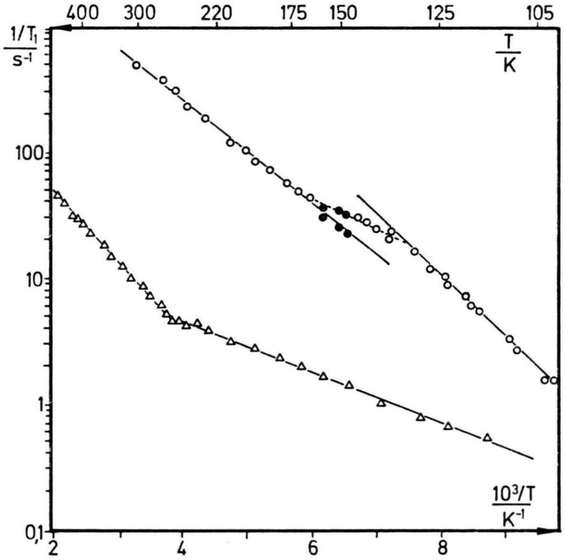

Fig. 3. The dependence of $1/T_1$ upon reciprocal temperature at 30 MHz for $Cu(4\text{-}CH_3\text{-}PNO)Cl_2 \cdot DMSO$ (○) and $Cu(PNO)Br_2$ (△).

Table 4. Singlet-triplet splitting in complexes with structural transformations and in instable addition compounds. PNO = pyridine-N-oxide, DMSO = dimethyl sulfoxide.

Compound	J/k [K]	Remarks
$Cu(PNO)Br_2$	1343	High temperature
	527	Low temperature
$Cu(PNO)Cl_2 \cdot DMSO$	872	High temperature
	1264	Low temperature
$Cu(PNO)Br_2 \cdot DMSO$	460	High temperature
	673	Low temperature
$Cu(4\text{-}CH_3{-}PNO)Cl_2 \cdot DMSO$	979	High temperature
	1151	Low temperature
$Cu(PNO)Cl_2 \cdot CH_3OH$	1364	Instable
$Cu(3\text{-}CH_3{-}PNO)Cl_2 \cdot CH_3OH$	1472	Instable
$Cu(3\text{-}CH_3{-}PNO)Br_2 \cdot CH_3OH$	1379	Instable

values of the exchange integral J, one for the high temperature modification and one for the low temperature modification.

IV. Discussion

The results indicate clearly that the anomalous magnetic behaviour of dimeric complexes is reflected by a strongly temperature dependent spin-lattice relaxation rate $1/T_1$. Compounds which possess a normal magnetic moment, on the other hand, display a constant relaxation rate over the temperature range investigated. As their magnetic moment is temperature independent, too, it may be concluded that for these "normal" complexes, the spectral density function of the electronic spin system is independent upon temperature in the region of nuclear Larmor frequency. The decisive question is, whether this condition is also fulfilled for the magnetically diluted dimeric complexes of this study. Only then Eq. (2) is applicable and the temperature dependence of $1/T_1$ can be correlated directly to the variation of populated triplet states.

Figure 2 reveals that the temperature dependence of the relaxation rate does not depend on the external field. Only the absolute value of $1/T_1$ may vary slightly indicating a small field dependence of the numerical constant K. No simple correlation to the magnitude of the external field could be found. As far as the calculation of the exchange integral J is concerned this effect is of no importance.

Over an extended temperature range, Eqs. (2) and (5), respectively, fit the experimental $1/T_1$ data. In Table 2 to 4 the values obtained for the singlet-triplet splitting energy are listed for a series of different complexes. The fitting itself cannot be considered as a sufficient proof of the aforementioned condition that the spectral density function is temperature invariant, but the agreement over such an extended temperature range is certainly an argument in favour. But a final decision may be possible by comparison of the results with J-values obtained from static measurements, i.e. from susceptibility data. For this purpose, several splitting energies reported in the literature are included in Tables 2 and 3. With the exception of the compound $Cu(PNO)Cl_2$ the agreement of the results derived from relaxation measurements and from conventional techniques is satisfactory. It may be concluded that relaxation measurements yield generally a reasonable value of the singlet-triplet splitting since agreement is realized for different types of dimeric complexes, where in the same time compounds with extremely different splitting energies were investigated. This may be considered as an experimental justification for the assumption of a temperature invariant spectral density function of electronic spin fluctuations.

The complex $Cu(PNO)Cl_2$ exhibits a significant discrepancy between the splitting energies obtained from T_1-measurements and from susceptibility data, respectively. We think that this is a consequence of the more chain-like structure of this complex with relative strong intermolecular exchange forces [21]. The compound is more likely a polymeric complex $[Cu(PNO)Cl_2]_n$. That may rise some doubts on both, the result derived from the relaxation measurement and the result from the susceptibility measurement. A final decision is not possible unless a direct measurement by inelastic neutron scattering has been performed.

The observed singlet-triplet splitting energies in N-oxide complexes (Table 3) can be interpreted in the following way. The influence of the different substituents on the exchange integral is mainly attributed to steric effects. Special importance possesses a substituent in ortho-position [22]. Both, the two methyl groups in LNO as well as the large ring system in QNO cause a dramatic increase of J. Probably, this is a consequence of a more favourable steric arrangement forced by the substituents, i.e. a perpendicular orientation of the aromatic system relative to the Cu-Cu-plane allowing maximum overlap with π-orbitals of the bridging oxygen. A single methyl group in ortho-position is obviously not large enough to yield a similar result. On the contrary, it seems to produce a destabilizing effect. Direct formation of the complex $Cu(2\text{-}CH_3\text{-}PNO)Cl_2$ is not possible. The exchange integral of the complex when obtained via the methanol adduct is extremely small. The diminished splitting energy of $Cu(4\text{-}PNO)Cl_2$, on the other hand, can be attributed to the electron-withdrawing influence of the nitro group.

Formation of solvent adducts with small molecules like H_2O and CH_3OH (Table 4) seems to increase the exchange integral. The additional ligand favours a more planar configuration of the bridging system. If the size of the solvent molecule becomes as large as DMSO, an opposite tendency can be observed. DMSO-adducts generally exhibit a smaller singlet-triplet splitting than the parent compounds. Steric interactions with the bridging ligand may be responsible.

The complex $Cu(4\text{-}CH_3\text{-}PNO)Cl_2 \cdot DMSO$ displays a very interesting behaviour at lower temperatures. A transition between two modifications occurs which takes place over a broad temperature range (Figure 2). The structural change is reversible and is accompanied by an alternation of the colour. The exchange integral of the low temperature modification is close to the value of the solvent-free complex. A decomposition of the adduct complex might be an explanation.

Let us finally discuss the usefulness of relaxation measurements at all in order to determine exchange integrals. There are some remarkable advantages. Firstly, the experimental procedure and the calculation of J are much simpler and, especially much faster as compared with the conventional techniques. Secondly, the error of the resulting J-values is mainly determined by the uncertainty of the temperature measurement and is relative small. Furthermore and thirdly, paramagnetic impurities, especially a certain amount of monomeric and/or polymeric Cu^{2+}-ions, do not influence the relaxation data. Special efforts towards the purification of the samples are not necessary. The complexes Cu(HQN)Cl and Cu(HQN)Br, for instance, crystallize always with a large amount of monomeric Cu^{2+}-ions [1]. Their dimeric structure could not be determined by magnetic measurements unambigously. The relaxation measurement, however, revealed the binuclear structure, and the splitting energy could be determined.

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