Figure 3. A part of spectrum of Maltol in CDCL₃: (a) normal spectrum; (b) the same part of the spectrum with ω_2 irradiation; and (c) difference of (a) and (b). Middle small singlet corresponds CHCL₃ in the solvent used.
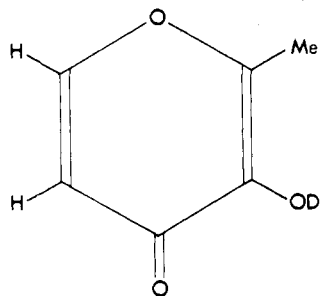

Figure 4.

ample. All traces are the result of five transient accumulations and are read out with absolute intensity mode.

As expected, the line corresponding to the regressive transition[4a] appears negative[3b] and the one due to the progressive transition appears positive, respectively.

The intensity of the partner line of the irradiated doublet can be interpreted in terms of the relaxation during a period between the time irradiated at ω_2 and that observed at ω_1.[5] The intensity estimated by making use of the equation developed by Wangsness and Bloch[6] under appropriate assumptions gives the same result as obtained from simple consideration based on the level population difference. However, the effect of the pulse at the frequency ω_1 must be small enough to act as the perturber for an unperturbed state which is established by the external field and the pulse at the frequency ω_2. Generally, the sensitivity seems still much higher in this method than conventional INDOR even under this condition.

In summary, the method described has benefits which include short experimental time, higher sensitivity, and ease of accumulation. There is promise of wide application to the analysis of many organic compounds, even in very dilute solutions.

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Compressed Tetragonal Distortion in Rb₂PbCu(NO₂)₆ at 295°K

Sir:

We wish to report the first example of *compressed* tetragonal distortion for six-coordinate Cu(II) with *equivalent* ligands. Single-crystal X-ray diffraction shows the rubidium lead hexanitrocuprate(II) crystals to be orthorhombic with space group, *Fmmm*. The crystallographic site symmetry for Cu(II) is D_{2h} (*mmm*), but two of the three pairs of Cu-N distances are equal within experimental error. Thus, Cu(II) has a compressed tetragonal environment with an average Cu-N bond length of 2.171 (5) Å for the long bonds and 2.063 (4) Å for the short bonds. The bond distances and bond angles are given in Table I, and the hexanitrocuprate(II) anion is shown in Figure 1.

Crystal data for the greenish black crystals are: a = 10.8296 (7), b = 10.8196 (7), and c = 10.6113 (7) Å; V = 1243.35 Å³ (λ = 0.70926 Å for the cell determination); orthorhombic, with space group *Fmmm* (D_{2h}^{23}, No. 69); four formula units (M = 717.7 daltons) per cell; D_x = 3.834 g cm⁻³; μ = 223.9 cm⁻¹ for Mo Kα radiation.

Intensity data were collected with an automated four-circle diffractometer, a NaI scintillation detector, and Mo Kα radiation with a Nb incident beam filter. The θ–2θ scan technique was used to measure all 5313 reflections out to 2θ = 90° ($\pm h$, $+k$, $\pm l$). The data were corrected for absorption and averaged to give 1427 independent reflections. Full-matrix least-squares refinement gave a conventional R factor of 0.026 based on all reflections.

Examples of Cu(II) in a compressed tetragonal environment cited by other authors are potassium tetrafluorocu-

Table I. Bond Distances (Å) and Bond Angles (deg) for Rb₂PbCu(NO₂)₆ at 295°K[a]

Cu–N(1)	2.063 (4)
Cu–N(2)	2.176 (5)
Cu–N(3)	2.166 (5)
N(1)–O(1)	1.241 (3)
N(2)–O(2)	1.241 (4)
N(3)–O(3)	1.250 (4)
Pb–O(1)	2.808 (3)
Pb–O(2)	2.789 (3)
Pb–O(3)	2.783 (3)
Rb–O(1)	3.168 (1)
Rb–O(2)	3.127 (1)
Rb–O(3)	3.145 (1)
O(1)–N(1)–O(1)	117.5 (3)
O(2)–N(2)–O(2)	116.6 (4)
O(3)–N(3)–O(3)	114.8 (4)

[a] Standard deviations of last significant figure are given in parentheses.
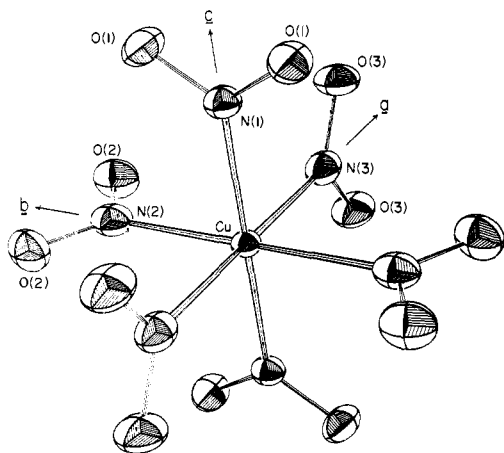
Figure 1. Hexanitrocuprate(II) anion showing atom numbering, thermal motion, and crystal axes. (Drawing produced by the computer program ORTEP; C. K. Johnson, Oak Ridge National Laboratory Report ORNL-3794, Oak Ridge, Tenn., 1965.)

prate(II),[1] barium hexafluorocuprate(II),[2] and bis(diethylenetriamine)copper(II) nitrate.[3] However, these are of limited value for studying Jahn–Teller effects since the Cu(II) ligands are not equivalent.[4]

In the fluoride complexes, K_2CuF_4 and $(BaF)_2CuF_4$, the long Cu–F distances are for four fluoride ions which bridge two Cu(II) ions while the short Cu–F distances are for nonbridging fluoride ions. The corresponding Ni(II) compounds K_2NiF_4[5] and $(BaF)_2NiF_4$[2] also show four long and two short Ni–F distances and, since six-coordinate Ni(II) is not a Jahn–Teller ion, the distortions observed in the Cu(II) complexes cannot be attributed to Jahn–Teller effects alone.

The bis(diethylenetriamine)copper(II) nitrate structure is not a good example of Jahn–Teller distortion since the ligands are tridentate and the $Cu^{(II)}$–N distances are determined in part by constraints imposed by the ligand geometry. The four long Cu–N bonds range from 2.17 (1) to 2.26 (2) Å, the two short Cu–N bonds average 2.01 Å, and all intraligand N–Cu–N angles are approximately 80°. The two short Cu–N distances correspond to the secondary amine nitrogen atoms and the four long bonds to primary amine atoms,[3] thus the ligands are again not equivalent. The corresponding Ni(II) compound shows a similar geometry with two short Ni–N (secondary) bonds and four long Ni–N (primary) bonds.[6] The same authors report the bis[di-(3-aminopropyl)amine]nickel(II) compound[6] which has two long and four short Ni–N bonds. They conclude that the Ni–N distances are strongly influenced by the ligand geometry.

In 1939 Van Vleck[7] stated, "It would be interesting if a physical case could be found where the cluster $X\cdot 6H_2O$ resonates through a variety of Jahn–Teller configurations, as then we would have a nice example of a characteristic quantum mechanical effect." We have sufficient evidence now to indicate that the cluster $Cu(NO_2)_6{}^{4-}$ is such an example since the presence or absence of a static distortion as well as the type of distortion depends on the counterion and on the temperature.

For example, both $K_2BaCu(NO_2)_6$[8] and $K_2CaCu(NO_2)_6$[9] crystallize in the same space group as $Rb_2PbCu(NO_2)_6$, but the CuN_6 environment is *elongated* tetragonal rather than *compressed* tetragonal in the presence of the K^+ counterion. A further example is provided by the observation that $K_2PbCu(NO_2)_6$ undergoes a reversible phase change from the cubic space group $Fm3$ with equal Cu–N distances[10] to the orthorhombic space group $Fmmm$ with

nonequivalent Cu–N distances below 280°K. Preliminary structural data for the orthorhombic phase indicate that the CuN_6 environment is *compressed* tetragonal with Cu–N distances of 2.07, 2.13, and 2.15 Å.[11] The corresponding nickel(II) compound, $K_2PbNi(NO_2)_6$, is cubic over the range of temperatures measured (130–295°K).[11] Thus, the changes in $M_2M'Cu(NO_2)_6$ structures can be attributed to the Jahn–Teller effect. Work is in progress which should provide precise structural data for $K_2PbCu(NO_2)_6$ below 280°K and for other crystals containing $Cu(NO_2)_6{}^{4-}$ and $Ni(NO_2)_6{}^{4-}$ clusters with various counterions.

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Effect of Micelles on the Rate and Stereochemistry of Solvolytic Displacement Reactions

Sir:

We wish to report the synthesis of a series of unusually reactive water soluble sulfonates (Ia–c) which has allowed us to study, for the first time, the effect of micelle formation[1] on the rate and stereochemistry of simple solvolytic displacement reactions. We have found that cationic micelles show little or no effect on the displacement reaction; in contrast, micelles formed from anionic surfactants bind Ia–c strongly, retard their rate of aqueous solvolysis by at least two orders of magnitude, and change the observed stereochemistry of displacement in Ib from 100% net inversion to 56% net inversion.[2]
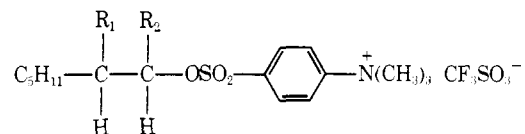
Ia, $R_1 = CH_3$; $R_2 = H$
Ib, $R_1 = H$; $R_2 = CH_3$
Ic, $R_1 = R_2 = H$

We chose I as the system for study[3] because these compounds are water soluble as well as structurally similar to the water insoluble sulfonates more traditionally used in solvolytic studies.[4] Also, sulfonates of structure I are surface active[5] and thus self-micellize and should bind well to micelles composed of other surfactants.

The nonmicellar solvolytic behavior of sulfonates I in water can be summarized as follows: (1) they exhibit conve-