Table I. Details of the UV–Visible Spectra (Peak Positions) for Relevant Complexes

complex	λ, nm (ε M^{-1} cm^{-1})
$[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ (I)	526 (135), 364 (263)
$[(NH_3)_3Co(\mu\text{-}CH_3CO_2)(\mu\text{-}OH)_2Co(NH_3)_3]^{3+}$ (II)	522 (111), 370 (234)
$[Cr(edta)(H_2O)]^-$ (III)[a]	540 (205), 390 (119)
$[Cr(Hedta)H_2O]$ (protonated III)[b]	540 (147), 390 (113)
$Co^{III}{}_2Cr^{III}$ complex (V)	534 (253), 367 (325)

[a] pH 4-5. [b] pH 1.9.

Table II. Acid Dissociation (K_a) Constants as pK_a Values for the H_2O Ligand of Cr(III) Complexes at 25 °C, I = 0.10 M ($NaClO_4$)[a]

complex	pK_a	complex	pK_a
$[Cr(edta)(H_2O)]^-$ (III)	7.39[b]	$[Cr(edtra)(H_2O)]$	6.25
$[Cr(medtra)(H_2O)]$ (IV)	6.25	complex V	5.76
$[Cr(hedtra)(H_2O)]$	6.02		

[a] Abbreviations: hedtra = *N*-(hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate; edtra = ethylenediamine-*N*,*N*′,*N*′-triacetate.
[b] See also: Schwarzenbach, G.; Heller, J. *Helv. Chim. Acta* 1951, *34*, 576. Furlani, C.; Morpurgo, G.; Sartori, G. *Z. Anorg. Allg. Chem.* 1960, *303*, 1.

The UV–visible spectrum gave a peak at 522 nm (ε 111 M^{-1} cm^{-1}) and a shoulder at 370 nm in agreement with a previous report.[2]

Spectra and pH Measurements. UV–visible spectra were recorded on Perkin-Elmer 550 and 554 spectrophotometers and IR spectra (KBr disks) on a Perkin-Elmer 598 instrument. All pH measurements were carried out with a Radiometer PHM 62 fitted with a Russell (CWR/322) glass electrode with a built-in Ag/AgCl reference.

Results and Discussion

Analyses were in accordance with the hexahydrate of the perchlorate salt of the $Co^{III}{}_2Cr^{III}$ complex as in V. The IR spectrum of $[Cr(Hedta)(H_2O)]$ gives bands at 1640 and 1743 cm^{-1} assigned to monodentate (O-coordinated) CO_2^- and free CO_2H groups.[12] The trinuclear complex V has bands at 1570 and 1630 cm^{-1} assigned to the μ-carboxylato and monodentate CO_2^- groups but no band at ~1740 cm^{-1} corresponding to free CO_2H, consistent with the formulation given in V.

Details of the UV–visible peak positions for relevant complexes are indicated in Table I. Spectra of the $Co^{III}{}_2$ and Cr^{III} chromophores are additive (±3%) over the range 350–650 nm (see Figure 1), and there is no evidence for interaction of the two chromophores.

Titration of a 5 × 10^{-4} M solution (25 mL) of the $Co^{III}{}_2Cr^{III}$ complex in 0.1 M $NaClO_4$ with 10^{-2} M NaOH at 25 °C using a glass electrode to monitor pH changes (range pH 4–11) gave only a single end point with acid dissociation pK_a = 5.76 (5.83 with I = 1.0 M ($NaClO_4$)). There is no uncoordinated CO_2H to titrate, and the pK_a observed is for the Cr(III)-coordinated H_2O. For comparison other relevant pK_a values are listed in Table II. The trends observed indicate a dependence on whether an uncoordinated CO_2^- arm is present or not. The presence of the positively charged $Co^{III}{}_2$ section of the complex may also be influential in bringing about a further lowering of the pK_a to 5.76.

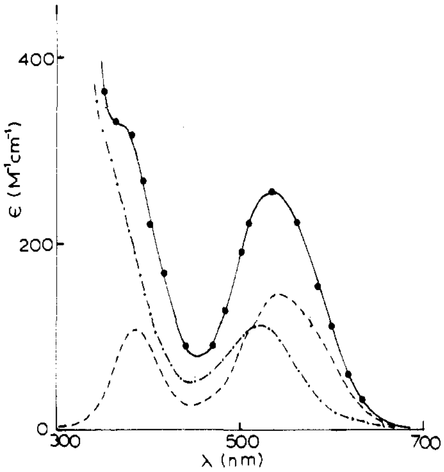

Figure 1. UV–visible spectra in 0.10 M $HClO_4$ for $(CH_3)_3Co(\mu\text{-}CH_3CO_2)(\mu\text{-}OH)_2Co(NH_3)_3{}^{3+}$ (–·–·) and $Cr(Hedta)(H_2O)$ (---) and the spectrum obtained on addition of these two (—), together with experimental points for the $Co^{III}{}_2Cr^{III}$ complex V.

The reactivity of the trinuclear complex V has been investigated by UV–visible spectrometer with (a) 0.10 M NCS^- in 0.10 M $HClO_4$ and (b) 1 M $CH_3CO_2^-/CH_3CO_2H$ at pH 5.0 and found to differ from that of the separate $Co^{III}{}_2$ and Cr^{III} complexes. Evidence obtained clearly indicates that the H_2O ligand attached to Cr(III) in V is no longer labile. With NCS^-, for example, the reaction of I (cleavage of a single μ-hydroxo bridge and coordination of NCS^-)[7] is complete within 25 min, and that of III (replacement of H_2O by NCS^-)[5] is rapid and complete in 1 min. In the case of the μ-acetato complex II, if there is a reaction, it is rapid and complete within 1 min of mixing. With the $Co^{III}{}_2Cr^{III}$ complex V, on the other hand, a slow process ($t_{1/2} \approx 3$ h) is observed with an ~25% increase in absorbance at ~540 nm. In the studies with 1 M acetate (pH 5.0) no reaction was observed with the $Co^{III}{}_2$ complexes I and II, and the reaction with the Cr^{III} complex III was observed to be rapid as reported elsewhere.[5] With V a slow reaction (monitored over 5 h) was observed, giving small (~4%) absorbance increases at ~540 nm and isosbestic points at 392, 455, and 530 nm. The only explanation of these observations is that slow anation at the H_2O coordination site of Cr(III) occurs in the case of V.

All the properties observed and reactions studied are consistent with the formation of a trinuclear $Co^{III}{}_2Cr^{III}$ complex as in V, where the unattached carboxylate of the edta forms a carboxylato bridge to $Co^{III}{}_2$ and results in a loss of lability of the H_2O coordinated to Cr^{III}.

Further support is also provided for the lability of the H_2O ligand in III resulting from the presence of the free uncoordinated carboxylate arm of the edta and its ability to form a transient chelate to Cr^{III}.

Acknowledgment. We thank the Swiss National Science Foundation for a fellowship to P.L.

Registry No. I, 22445-08-5; III, 15955-81-4; V, 84895-75-0.

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(12) See also: Scott, K. L.; Wieghardt, K.; Sykes, A. G. *Inorg. Chem.* **1973**, *12*, 655.
(13) Wharton, R. K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2404.

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Uniaxial Stress Measurements on $Rb_2BaCu(NO_2)_6$

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Received July 14, 1982

$Rb_2BaCu(NO_2)_6$ is one of a series of $M_2M'Cu(NO_2)_6$ compounds in which the crystallographic site symmetry of

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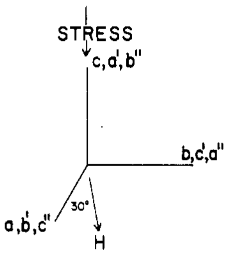

Figure 1. Representation of stress, magnetic field, and lattice axes. The three lattice orientations are *a*, *b*, *c* (C), *a'*, *b'*, *c'* (C'), and *a''*, *b''*, *c''* (C''). The magnetic field (*H*) is perpendicular to *c* and approximately 30° from *a*. Stress is applied along *c*.

Cu(II) is $D_{2h}(mmm)$, with two of the three pairs of Cu–N distances equal within experimental error. In both $K_2PbCu(NO_2)_6$ and $Rb_2PbCu(NO_2)_6$, CuN_6 is compressed tetragonally in the orthorhombic phase while $K_2BaCu(NO_2)_6$, $K_2CaCu(NO_2)_6$, $K_2SrCu(NO_2)_6$, and $Rb_2BaCu(NO_2)_6$ have elongated-tetragonal CuN_6 groups.[2] All the orthorhombic $M_2M'Cu(NO_2)_6$ compounds we have studied show a tendency to twin. The lattices have a common (110) boundary,[3] but the relative population of the lattices varies with the crystal, temperature, and applied stress. A previous report from this laboratory[4,5] described the effect of uniaxial stress on multilattice orthorhombic crystals of $Rb_2PbCu(NO_2)_6$ and $K_2PbCu(NO_2)_6$ in which the CuN_6 configuration is compressed tetragonally. The purpose of the present study was to determine whether ferroelasticity[6,7] is a general property of the orthorhombic phase of $M_2M'Cu(NO_2)_6$ compounds by making uniaxial stress measurements on multilattice orthorhombic crystals of $Rb_2BaCu(NO_2)_6$, a representative of $M_2M'Cu(NO_2)_6$ compounds with an elongated-tetragonal CuN_6 configuration.

Experimental Section

Crystals of $Rb_2BaCu(NO_2)_6$ (0.2–0.5 mm) were grown by a published agar gel technique.[8] Crystals chosen for stress measurements had large, smooth, well-formed {100} faces with very small {110} and {111} faces. The apparatus and procedure for stress measurements were the same as those used for $Rb_2PbCu(NO_2)_6$.[4] Values of $g_\parallel$ and $g_\perp$ were obtained before carrying out stress measurements by aligning the multilattice crystal in the spectrometer with the magnetic field parallel to one of the crystal axes (e.g., *c'* in Figure 1). The resulting two-line spectrum gave values of $g_\parallel = 2.250$ and $g_\perp = 2.063$, which are typical for elongated-tetragonal CuN_6 configurations.[9]

Results and Discussion

EPR spectra for $Rb_2BaCu(NO_2)_6$ indicate that all three of the lattice orientations shown in Figure 1 are present. In the following discussion we will refer to the orientations shown in Figure 1 as C, C', and C'', respectively. The elongated Cu–N axis for each lattice will be along one of three mutually perpendicular directions (*c*, *c'*, *c''* axes) in the multilattice crystal. For most crystal orientations the angle between the magnetic field and the *c* axis will be different for each of the three lattice orientations. As a result, the spectrum will consist of three lines with each line representing contributions from one of the three lattices (Figure 2a). The intensity of each line is proportional to the population of the corresponding lattice orientation.

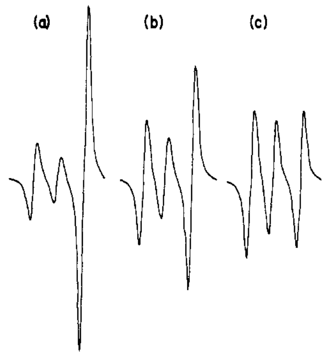

Figure 2. EPR spectra at 300 K of $Rb_2BaCu(NO_2)_6$ crystal 17 oriented as shown in Figure 1: (a) no stress; (b) 451 N cm^{-2} stress; (c) 689 N cm^{-2} stress. Line widths range from 18 to 26 G.

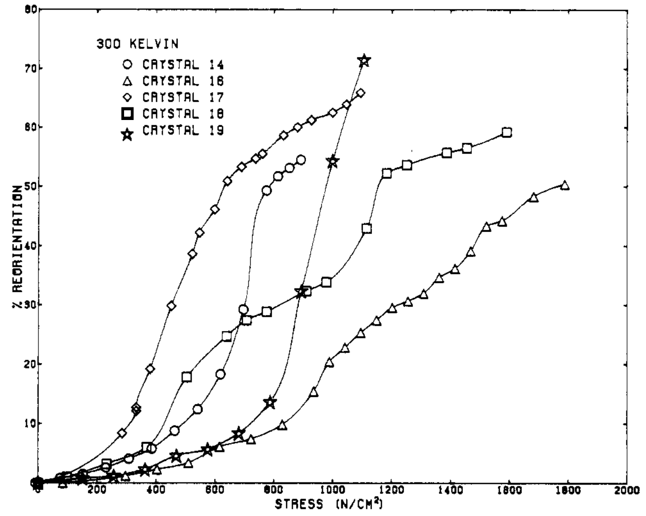

Figure 3. Percent reorientation vs. stress for five $Rb_2BaCu(NO_2)_6$ crystals at 300 K. Cross-sectional areas of crystals 14, 16, 17, 18, and 19 are 0.13, 0.092, 0.21, 0.072, and 0.046 mm², respectively.

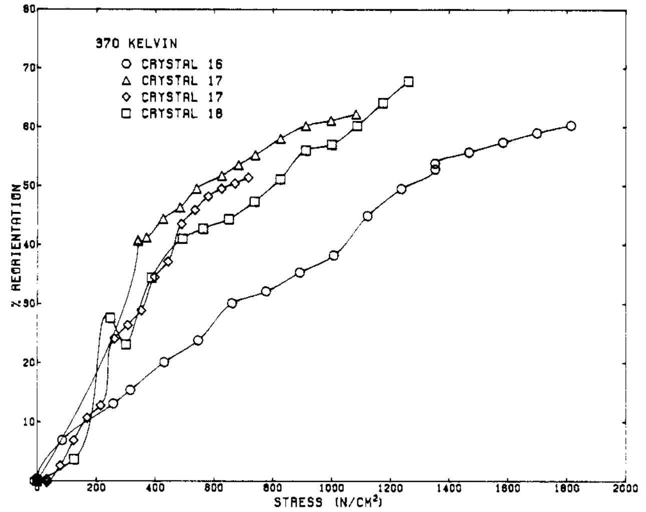

Figure 4. Percent reorientation vs. stress for three $Rb_2BaCu(NO_2)_6$ crystals at 370 K.

The crystal is aligned in the spectrometer with (001) vertical and the horizontal field perpendicular to that axis and ap-

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(2) M. D. Joesten, Shozo Takagi, and P. G. Lenhert, *Inorg. Chem.*, **16**, 2680 (1977) and references cited therein.

(3) Shozo Takagi, M. D. Joesten, and P. G. Lenhert, *Chem. Phys. Lett.*, **34**, 92 (1975).

(4) M. D. Joesten, F. D. Srygley, and P. G. Lenhert, *Solid State Commun.*, **32**, 725 (1979).

(5) In ref 4 the (110) common boundary is incorrectly referred to as (100).

(6) K. Aizu, *Phys. Rev. B: Solid State*, **2**, 754 (1970).

(7) S. C. Abrahams, *Mater. Res. Bull.*, **6**, 881 (1971).

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(9) D. Reinen and C. Friebel, *Struct. Bonding (Berlin)*, **37**, 1 (1979).

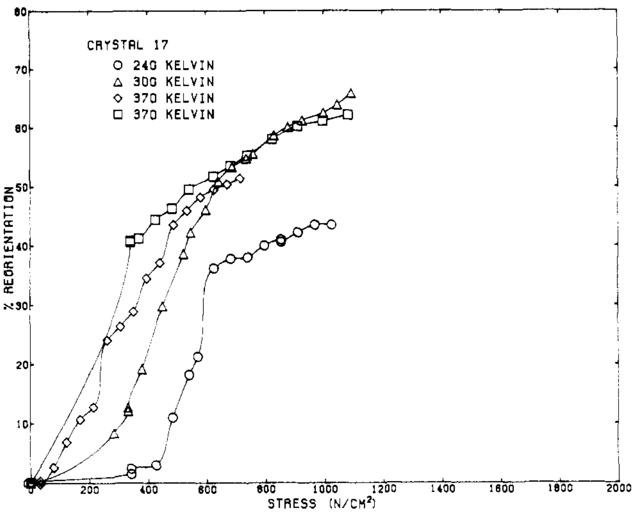

Figure 5. Percent reorientation vs. stress for $Rb_2BaCu(NO_2)_6$ crystal 17 at four temperatures.

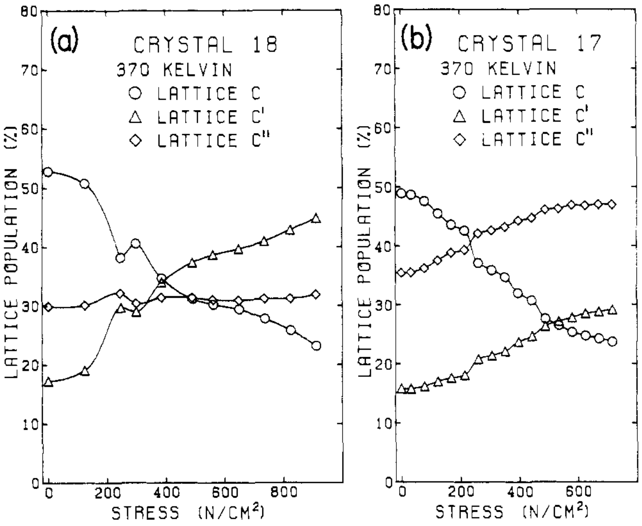

Figure 6. (a) Change in lattice population of crystal 18 with increase in stress. Note lattice C'' is not affected. (b) Change in lattice population of crystal 17 with increase in stress. Both lattice C' and lattice C'' show similar changes.

proximately 30° from the (100) axis and 60° from the (010) axis. The *c* axes of some domains will be along (001) while those for other domains (*c*', *c*'' in Figure 1) will be along (010) and (100). The field will then be perpendicular to *c*, at a 60° angle with *c*', and at a 30° angle with *c*''. The spectra in Figure 2 are for this orientation.

As stress is applied along (001), the domains with *c* along this direction have their *c* axis converted to an *a*' or a *b*'' axis while *a* or *b* is converted to a *c*'' or *c*' axis. This is equivalent to a reorientation of the C lattice to C' or C''. Figure 2 illustrates the magnitude of the spectral change for different stresses. Line widths and line shapes of the three lines (Figure 2) are similar for different crystals and orientations and also are comparable to those expected for Cu(II) when hyperfine structure is absent. The peak to peak height of a given line was divided by the total peak to peak height for all three lines to give the fractional population of that lattice orientation. Percent reorientation was obtained by observing the shift in population of the C lattice orientation. If *f* represents the fraction of the crystal domains with the C orientation, then

$$\text{percent reorientation} = \frac{f_i - f}{f_i} \times 100$$

where f_i is the initial fractional population of that lattice orientation in the crystal.

Figure 3 is a plot of percent reorientation vs. stress for five crystals of $Rb_2BaCu(NO_2)_6$ at 300 K, and Figure 4 is a similar plot for three crystals at 370 K. The data illustrate that the magnitude of stress required for reorientation at a given temperature varies from crystal to crystal. Generally, the stress required for reorientation increases with a decrease in temperature as illustrated in Figure 5 for crystal 17. The range of stress values required for reorientation (200–600 N cm^{-2}) is similar to that found for compressed-tetragonal $Rb_2PbCu(NO_2)_6$.[4]

Sometimes there is a preference during reorientation for the *c* axis to convert to either *a*' or *b*'' rather than an equal conversion to each. This is illustrated in Figure 6a, where lattice orientation C'' undergoes little change in population. Figure 6b shows about the same increase in population of both of the lattice orientations C' and C''.

In summary, the data presented here and in ref 4 indicate that uniaxial stress reorients multilattice crystals of the orthorhombic phase of $M_2M'Cu(NO_2)_6$ compounds. Hence ferroelasticity appears to be a common property for this series.

Acknowledgment. We wish to thank Professor L. K. Wilson for the use of his EPR spectrometer and the National Science Foundation (Grant No. CHE 77-09788) for support.

Registry No. $Rb_2BaCu(NO_2)_6$, 60674-39-7.