

Ln_2BaZnO_5 and $Ln_2BaZn_{1-x}Cu_xO_5$: A Series of Zinc Oxides with Zinc in a Pyramidal Coordination

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A series of zinc oxides Ln_2BaZnO_5 has been synthesized for $Ln = Sm, Eu, Gd, Dy, Ho,$ and Y . These phases are orthorhombic and isostructural with the copper compounds Ln_2BaCuO_5 previously described, as shown from the structural study of one member Y_2BaZnO_5 . In this structure, whose framework is built up from edge- and face-sharing LnO_7 polyhedra, the Zn^{2+} ions exhibit an unusual pyramidal coordination ZnO_5 . The solid solution $Y_2BaZn_{1-x}Cu_xO_5$ has been studied by infrared spectroscopy and electron spin resonance (ESR). The distorted square-based pyramidal configuration of Zn^{2+} and Cu^{2+} is confirmed. The ESR spectra of diluted samples exhibit a hyperfine structure and are typical of individual Cu(II) ions. For higher Cu(II) contents, they exhibit an anisotropic broad signal which is interpreted in terms of Cu-Cu interactions.

Introduction

Three series of oxides, corresponding to the general formula Ln_2BaMO_5 ($M = Cu$ or Zn), have recently been isolated and characterized (1-3). Copper oxides form two different structural families depending on the nature of the lanthanide ions. The lanthanum and neodymium oxides $Ln_{2-x}Ba_{1+x}Cu_{1-x/2}O_{5-x}$ are in fact nonstoichiometric, and built up from layers of edge- and face-sharing LnO_8 polyhedra which are held together by Ba^{2+} ions and Cu(II) ions in square planar coordination. In copper oxides of the other lanthanides Ln_2BaCuO_5 ($Ln = Sm, Eu, Gd, Dy, Ho, Er, Yb$) and of yttrium, copper exhibits a distorted square-based pyramidal coordination but does not participate directly in the three-dimensional framework which can be considered as built

up from corner and face-sharing LnO_7 polyhedra. Substitution of zinc for copper in the first class did not give solid solutions owing to the inability of zinc to take a planar coordination, but Ln_2BaZnO_5 oxides ($Ln = La, Nd$) were isolated with structures closely related to that of $Ln_{2-x}Ba_{1+x}Cu_{1-x/2}O_{5-x}$: their framework is built up from identical layers of LnO_8 polyhedra, but the zinc ions which ensure the cohesion between these layers exhibit a tetrahedral coordination.

Distorted tetragonal pyramidal coordination of zinc seems very rare relative to tetrahedral or trigonal bipyramidal, and only some complexes are known at the present time (4-5). Thus, the present work deals with the substitution of zinc for copper in the second family of the copper oxides and especially with the compounds Ln_2BaZnO_5 ($Ln = Sm, Eu, Gd, Dy, Ho,$ and yttrium).

Experimental

Synthesis. Mixtures of Ln_2O_3 ($Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb$) or Y_2O_3, ZnO (and sometimes CuO), and $BaCO_3$ were heated in air in platinum crucibles, first for 12 hr at $900^\circ C$, then for 24 hr or more at $1100^\circ C$ and finally quenched at room temperature.

Characterization. The X-ray diffraction patterns were registered up to $\theta = 46^\circ$ with a Philips powder diffractometer using $CuK\alpha$ radiation. The intensities were measured using both counter and graphical measurements. Calculations of intensities were made with the scattering factors of ionic species from Cromer and Waber (6) and corrected for anomalous dispersion (7). Least-squares refinements were made with all reflections using a program which takes account of the overlapping of the peaks (8).

Infrared spectra were obtained with a Beckman spectrometer using KBr , in the range $800\text{--}200\text{ cm}^{-1}$. The ESR study was made with a Bruker ER 200 X-band spectrometer ($f \sim 9.5\text{ GHz}$). This spectrometer is supplied with a double cavity which can give simultaneously the spectrum of the sample and of a standard (strong pitch $g = 2.0028$).

Results and Discussion

Six new phases Ln_2BaZnO_5 were isolated, in the form of light gray powders for $Ln = Sm, Eu, Gd, Dy, Ho, \text{ and } Y$. They are isotypic of the copper oxides, Ln_2BaCuO_5 , previously described (2). The X-ray diffractograms of these phases could thus be indexed in a similar orthorhombic cell containing 4 Ln_2BaZnO_5 units (Table I). The cell parameters of these compounds decrease regularly with the size of the Ln^{3+} ion. The reflexion conditions, similar to those of copper oxides ($h0l: h + l = 2n$; $0kl: k = 2n$), lead to two possible space groups: $Pbn2_1$ and $Pbnm$. Attempts to pre-

TABLE I
CRYSTAL DATA AND DENSITIES OF THE OXIDES
 A_2BaZnO_5

Compound	a (Å)	b (Å)	c (Å)	d_{exp}	d_{calc}
Y_2BaZnO_5	7.068(3)	12.324(4)	5.706(2)	6.20	6.16
Sm_2BaZnO_5	7.207(5)	12.593(8)	5.811(2)	7.36	7.35
Eu_2BaZnO_5	7.184(2)	12.537(5)	5.793(2)	7.51	7.47
Gd_2BaZnO_5	7.159(3)	12.493(7)	5.775(2)	7.67	7.68
Dy_2BaZnO_5	7.083(4)	12.358(8)	5.721(3)	7.97	8.06
Ho_2BaZnO_5	7.063(4)	12.318(6)	5.704(2)	8.13	8.20

pare the oxides corresponding to $Ln = Er$ and Yb were unsuccessful contrary to the case of copper; neither could Tb oxide be synthesized.

Structural Study of Y_2BaZnO_5

The structural study of one phase of this series, Y_2BaZnO_5 , was undertaken in order to confirm its similarity with the copper oxides and especially to verify the tetragonal pyramidal coordination of Zn^{2+} . The intensities of the first 76 peaks, i.e., 214 reflections were measured and used in a calculation of intensities in the most symmetrical space group $Pbnm$ (in order to limit the number of variable parameters). The different atoms were first located in positions similar to those obtained from the structural study of Y_2BaCuO_5 . In this case the discrepancy R factor was about 0.10. Successive refinements of the atomic coordinates and of isotropic thermal parameters lowered the R factor to $R = 0.065$. The final coordinates (Table II) are very close to those observed for Y_2BaCuO_5 and Gd_2BaCuO_5 (2). Calculations in the less symmetrical space group ($Pbn2_1$) do not lead to a significant lower value of the R factor: $R = 0.062$.

Thus it is confirmed that the structure of these compounds is very similar to that of Ln_2BaCuO_5 previously described: it consists of edge and face-sharing distorted monocapped trigonal prisms LnO_7 which form a three-dimensional framework as

TABLE II
VARIABLE PARAMETERS OBTAINED AFTER
STRUCTURAL REFINEMENTS FOR THE OXIDE
 Y_2BaZnO_5 (SPACE GROUP $Pbnm$)

Atom	Site	x	y	z	B (\AA^2)
Y ₁	4(c)	0.122(1)	0.2937(5)	1/4	0.7(2)
Y ₂	4(c)	0.3956(9)	0.0734(5)	1/4	0.2(1)
Ba	4(c)	0.9233(5)	0.9004(3)	1/4	1.1(1)
Zn	4(c)	0.6942(9)	0.6505(6)	1/4	0.8(2)
O ₁	8(d)	0.167(3)	0.437(2)	-0.013(2)	0.3(6)
O ₂	8(d)	0.355(4)	0.243(1)	0.480(3)	1.5(8)
O ₃	4(c)	0.075(4)	0.106(2)	1/4	0.1(6)

shown on Figs. 1 and 2. This framework delimits cavities where the barium and zinc ions are located. Barium ions are surrounded by 11 oxygen atoms, while Zn^{2+} ions are located in a distorted square-based pyramid (Fig. 2).

The interatomic distances (Table III) are very close to those observed in the copper compounds: they range from 2.20 to 2.48 \AA for Y–O, from 2.75 to 3.29 \AA for Ba–O, and from 1.98 to 2.05 \AA for Zn–O. However,

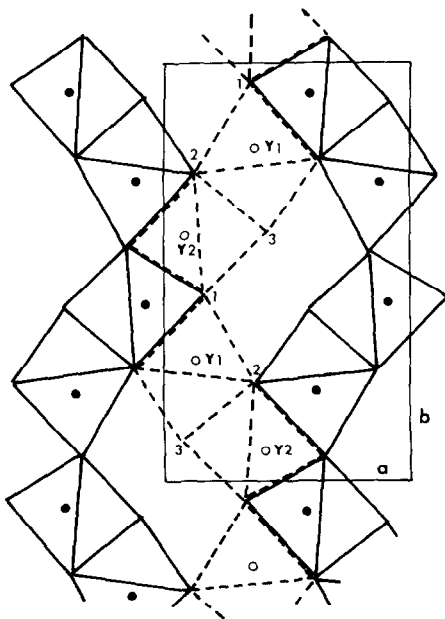


FIG. 1. Projection in the (001) plane of the linkage of YO_7 polyhedra at $z = \frac{1}{4}$ (broken line) and $z = \frac{3}{4}$ (solid line).

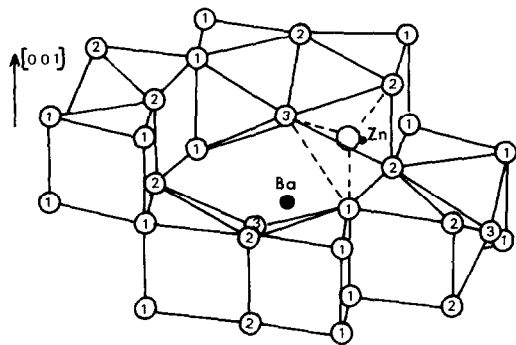


FIG. 2. Perspective view of some edge- and face-sharing monocapped trigonal prisms YO_7 , showing cavities where Zn^{2+} and Ba^{2+} ions are located.

the ZnO_5 polyhedron (Fig. 3a) is rather different from the CuO_5 polyhedron (Fig. 3b). The “out-of-plane” Cu–O distance (2.29 \AA) is indeed much greater than the corresponding Zn–O distance (1.98 \AA); it results that the “out-of-plane” Cu–O distance is greater than the “in-plane” Cu–O distances while the contrary is observed for the ZnO_5 polyhedron.

Such a coordination of the Zn^{2+} ions is rather surprising in oxides. In order to confirm this structural powder work, in which the oxygen positions cannot be determined very accurately, and also in order to bring an additional contribution to the knowledge of the Ln_2BaCuO_5 oxides, we have studied the solid solution $Y_2BaZn_{1-x}Cu_xO_5$ by infra-

TABLE III
INTERATOMIC DISTANCES

M–O	Distance (\AA)	M–O	Distance (\AA)
Y(1)–O(1)	$2.34(2) \times 2$	Ba–O(1)	$3.29(2) \times 2$
Y(1)–O(2)	$2.20(2) \times 2$	Ba–O'(1)	$3.02(2) \times 2$
Y(1)–O'(2)	$2.48(2) \times 2$	Ba–O(2)	$2.82(2) \times 2$
Y(1)–O(3)	$2.34(2) \times 1$	Ba–O'(2)	$3.06(2) \times 2$
Y(2)–O(1)	$2.30(2) \times 2$	Ba–O(3)	$2.854(1) \times 2$
Y(2)–O'(1)	$2.35(2) \times 2$	Ba–O'(3)	$2.75(2) \times 1$
Y(2)–O(2)	$2.49(2) \times 2$	Zn–O'(1)	$1.99(2) \times 2$
Y(2)–O(3)	$2.30(3) \times 1$	Zn–O'(2)	$2.05(2) \times 2$
		Zn–O(3)	$1.98(3) \times 1$

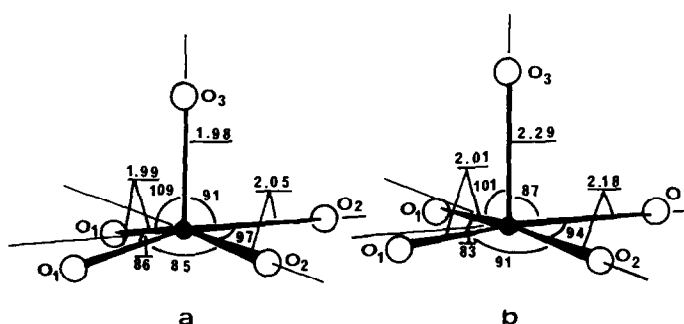


FIG. 3. (a) ZnO₅ polyhedron, (b) CuO₅ polyhedron.

red spectroscopy and electron spin resonance.

The Solid Solution $Y_2BaZn_{1-x}Cu_xO_5$ ($0 \leq x \leq 1$)

The complete solid solution between Y₂BaZnO₅ and Y₂BaCuO₅ has been synthesized; the green color of the powders, due to the presence of copper, increases with x . The parameters of the orthorhombic cell exhibit a regular change as a function of x (Fig. 4), it is worthy of note that, except "a", "b" and "c" parameters decrease as the copper content increases.

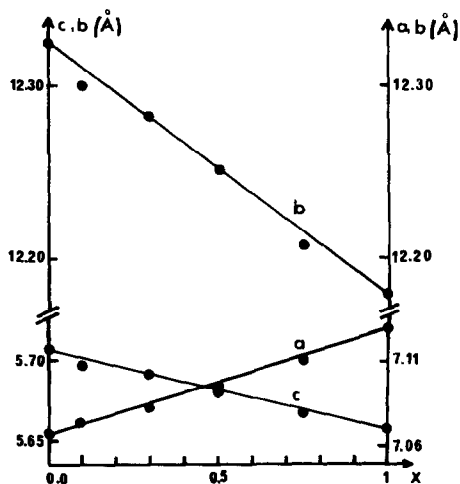


FIG. 4. Evolution of the cell parameters of the solid solution compounds Y₂BaZn_{1-x}Cu_xO₅ as a function of x .

Infrared spectra. In order to determine the bands corresponding to Cu-O and Zn-O vibrations in these oxides, the ir spectra of three oxides—Y₂BaCuO₅, Ho₂BaCuO₅, and Y₂BaZnO₅—were determined (Fig. 5). The comparison of the spectra of yttrium and holmium compounds shows that the bands at 610, 505, and 325 cm⁻¹ can be attributed without ambiguity to Cu-O vibrations. The other bands correspond to Y-O, Ba-O, and Ho-O, Ba-O, vibrations, respectively. The Y-O bands can be identified since they are shifted by replacing yttrium by holmium. By comparing Y₂BaCuO₅ and Y₂BaZnO₅ spectra, we can identify the bands at 585, 485, and 300 cm⁻¹

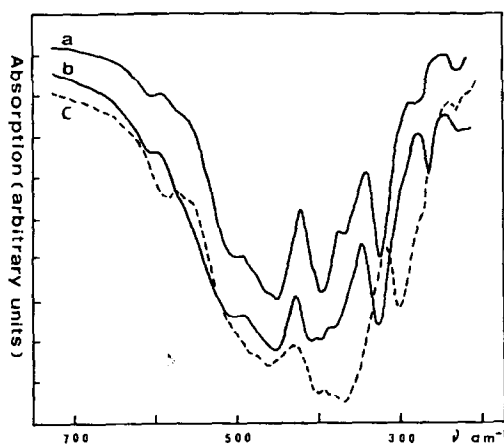


FIG. 5. Infrared spectra: (a) Y₂BaCuO₅, (b) Ho₂BaCuO₅, (c) Y₂BaZnO₅.

as corresponding to Zn–O vibrations. It is thus clear that the ZnO_5 and CuO_5 polyhedra are similar in both structures, the lower frequencies observed for Zn–O bands being in agreement with the greater atomic mass of Zn. The possibility of localization of Zn^{2+} and Cu^{2+} on the same type of site is confirmed by the spectra of different compositions of the solid solution which exhibit intermediate frequencies; this is the case for $\text{Y}_2\text{BaZn}_{0.5}\text{Cu}_{0.5}\text{O}_5$ which exhibits three bands at 600, 500, and 310 cm^{-1} . The band at about 300 cm^{-1} can be associated with the band observed in the region 330–280 cm^{-1} in some six and five coordinated (tetragonal pyramid) copper complexes involving oxygen coordination (9). In copper complexes with Cu in trigonal bipyramidal coordination, this band was observed at lower frequencies (about 260 cm^{-1} (9) thus the infrared spectra seem to be more in agreement with a tetragonal pyramidal environment of copper than with a trigonal bipyramidal environment.

ESR spectra. The ESR spectra of five coordinated copper complexes are now well understood as far as two limiting square pyramidal and trigonal bipyramidal forms are concerned. The two forms can easily be differentiated by ESR since $g_{\perp} > g_{\parallel} \approx 2.00$ and $|A_{\parallel}| \approx |A_{\perp}| \approx 60\text{--}100 \times 10^{-4} \text{ cm}^{-1}$ for the trigonal environment (10–14) and $g_{\parallel} > g_{\perp}$ with $|A_{\perp}| \ll |A_{\parallel}| \approx 120\text{--}150 \times 10^{-4} \text{ cm}^{-1}$ for square pyramidal complexes (9 – 15 – 19). Some magnetically diluted and undiluted copper complexes with intermediate configurations have also been studied (20–24).

The formation of the solid solution $\text{Y}_2\text{BaZn}_{1-x}\text{Cu}_x\text{O}_5$ allows to assume that copper replaces zinc on the same sites but likely keeps the geometrical distortion which corresponds to the undiluted oxide. The ESR study of diluted sample could thus bring some information on the copper coordination in these phases.

The room-temperature spectrum of a sample containing less than 1% Cu is re-

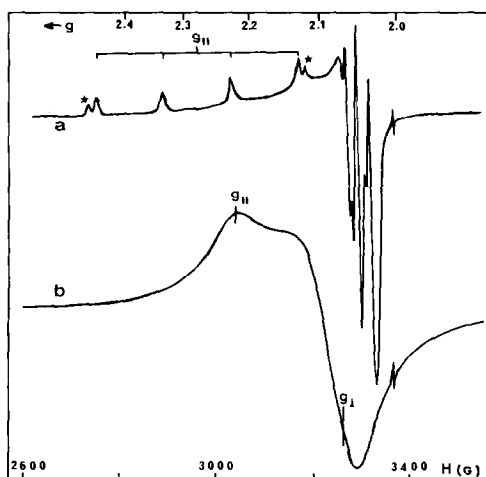


FIG. 6. Room-temperature ESR spectra: (a) $\text{Y}_2\text{BaZn}_{0.99}\text{Cu}_{0.01}\text{O}_5$, (b) Y_2BaCuO_5 . The small signal in high field is the standard signal (strong pitch $g = 2.0028$).

corded on Fig. 6a. It is typical of an axially distorted copper site as found in the structural study of Y_2BaCuO_5 (2) (out-of-plane Cu–O distance: 2.29 Å; in-plane Cu–O distances (mean value): 2.09 Å). The spectrum is well resolved, so, the parallel part can be easily interpreted and the g_{\parallel} and $|A_{\parallel}|$ values calculated. The satellites, marked by a star, are due to the ^{65}Cu isotope of relative abundance of 30.9%. The experimental g_{\parallel} and $|A_{\parallel}|$ values are $g_{\parallel} = 2.275$; $|A_{\parallel}| = 147.5$ and $158 \times 10^{-4} \text{ cm}^{-1}$ for the ^{63}Cu and ^{65}Cu isotopes, respectively. The ratio of the hyperfine constant (1.072) agrees very well with the nuclear magnetic moment ratio (1.071) of the two isotopes. The interpretation of the perpendicular part of the spectrum is difficult in spite of the existence of a hyperfine structure. Six peaks are indeed observed which may result from the superposition of two sets of four peaks which could be due to two different g values. Simulations of the spectra have been carried out in order to evaluate the values of the g tensor and of the hyperfine constant but they were always unsuccessful. Thus it is not possible to know if one or two g values occur in the

perpendicular part of the spectrum. If two g values appear they cannot differ by more than 0.01 with a mean g value of about 2.05. This could be due to the omission of the second order terms and of the nuclear quadrupole effect Q in our calculations. The value of the hyperfine constant can be evaluated in the range $15\text{--}25 \times 10^{-4} \text{ cm}^{-1}$ so the second-order terms would not be of great influence on the field dependence of the hyperfine components. Quadrupole interactions which induce forbidden transitions ($\Delta M_I \neq 0$) can participate in a significant manner in the perpendicular part of the spectrum involving the formation of extra peaks. In some copper compounds the value of Q has been found to be $6\text{--}8 \times 10^{-4} \text{ cm}^{-1}$ (25–27); if such a value occurs in our compounds, Q cannot be neglected compared to A_{\perp} . The spectra registered at 77 and at 4.2°K do not exhibit any significant change so that more complex simulations will be necessary to complete the interpretation of the spectrum of this compound. Although the spectrum could not be completely interpreted, it is confirmed that the CuO_5 polyhedron and consequently the ZnO_5 polyhedron are more a slightly distorted square based pyramid than a trigonal bipyramid. Moreover, the G parameter defined by $G = (g_{\parallel} - 2)/(g_{\perp} - 2) > 4$ (15) shows that the spectrum is typical of individual Cu(II) ions in pyramidal environment with no Cu–Cu interactions.

As soon as copper content increases up to 10%, a change is observed in the ESR spectrum. A new line spreads out due to the vanishing of the hyperfine structure and the broadening of the signal. A typical curve is given in Fig. 6b for Y_2BaCuO_5 . The g values calculated from this spectrum are $g_{\parallel} \approx 2.22$ and $g_{\perp} \approx 2.07$. These results are in agreement with the structural results; two magnetically nonequivalent CuO_5 polyhedra are observed which are located at the same level with regard to the x_0y plane; their long axis (Cu–O “out-of-plane” bond)

form an angle $2\alpha \approx 50^\circ$. So, the marked broadening of the signal could result from the interaction between these non equivalent Cu(II) ions; moreover the separate g values may converge to give new g values. The nonisotropic spectrum observed here may result from the exchange coupling between noncrystallographically equivalent ions; if this is true, the observed g_{\perp} may be larger than the local g_{\perp} and the observed g_{\parallel} may be smaller than the local g_{\parallel} , leading to $G < 4$. The experimental $G = 3.14$ confirms this point of view. The observed g values may be related to the site g values with a relatively good approximation by using the expressions

$$\begin{aligned} g_1^2 &= g_{\parallel}^2 \cos^2\alpha + g_{\perp}^2 \sin^2\alpha \\ g_2^2 &= g_{\parallel}^2 \sin^2\alpha + g_{\perp}^2 \cos^2\alpha \end{aligned}$$

where 2α is the angle defined above. Using $2\alpha = 50^\circ$ and assuming that $g_1 = g_{\parallel}$ and $g_2 = g_{\perp}$ as it appears if we do $2\alpha = 0^\circ$ (crystallographically equivalent sites), we obtain $g_{\parallel} = 2.23$ and $g_{\perp} \approx 2.09$. These values are consistent with those observed on the spectrum for 100% Cu.

Conclusion

We have synthesized $\text{Ln}_2\text{BaZnO}_5$ oxides characterized by an unusual coordination of Zn^{2+} . The formation of a continuous solid solution with the copper oxide $\text{Ln}_2\text{BaCuO}_5$ led us to an investigation of the copper coordination by ir and ESR methods. The distorted square pyramidal coordination of copper in these phases is confirmed. The ESR spectra of the diluted oxides show that the unpaired electron of $3d^9$ Cu(II) is located in the $d_{x^2-y^2}$ orbital. However, if two g values occur in the perpendicular part of the spectrum, the d_{z^2} orbital would be mixed with the $d_{x^2-y^2}$ orbital in the ground state. The knowledge of the $d_{x^2-y^2}$ orbital percentage in the ground state and of the reduction factors needs further investigation in ESR and visible spectroscopy.

References

1. C. MICHEL, L. ER-RAKHO, AND B. RAVEAU, *J. Solid State Chem.* **39**, 161 (1981).
2. C. MICHEL AND B. RAVEAU, *J. Solid State Chem.* **43**, 173 (1982).
3. C. MICHEL, L. ER-RAKHO, AND B. RAVEAU, *J. Solid State Chem.* **42**, 176 (1982).
4. M. BONAMICO, G. MAZZIONE, A. VACIAGO, AND L. ZAMBONELLI, *Acta Crystallogr.* **19**, 898 (1965).
5. D. HALL AND F. H. MOORE, *J. Chem. Soc. A* 1822 (1966).
6. D. T. CROMER AND J. T. WABER, *Acta Crystallogr.* **18**, 104 (1965).
7. D. T. CROMER, *Acta Crystallogr.* **18**, 17 (1965).
8. C. C. PHAM, J. CHOISNET, AND B. RAVEAU, *Bull. Acad. R. Belg. Sci.* **61**, 473 (1975).
9. A. A. G. TOMLINSON AND B. J. HATHAWAY, *J. Chem. Soc. A* 2578 (1968).
10. B. J. HATHAWAY AND D. E. BILLING, *Coord. Chem. Rev.* **5**, 143 (1970).
11. B. J. HATHAWAY, D. E. BILLING, R. J. DUDLEY, R. J. FEREDAY, AND A. A. G. TOMLINSON, *J. Chem. Soc. A*, 806 (1970).
12. B. A. GOODMAN AND J. B. RAYNOR, *Adv. Inorg. Chem. Radiochem.* **13**, 135 (1970).
13. R. BARBUCCI AND M. J. CAMPBELL, *Inorg. Chim. Acta I* **15**, 15 (1975).
14. R. BARBUCCI, A., BENCINI, AND D. GATTESCHI, *Inorg. Chem.* **16**, 2117 (1977).
15. A. A. G. TOMLINSON AND B. J. HATHAWAY, *J. Chem. Soc. A* 1685 (1968).
16. A. A. G. TOMLINSON AND B. J. HATHAWAY, *J. Chem. Soc. A* 1905 (1968).
17. D. K. JOHNSON, H. J. STOKLOSA, J. R. WASSON, AND G. L. SEEBACH, *J. Inorg. Nucl. Chem.* **37**, 1397 (1975).
18. R. I. BELFORD AND C. D. DUAN, *J. Magn. Reson.* **29**, 293 (1978).
19. B. A. SASTRY, S. MD. ASADULLAH, G. PONTICELLI, AND M. MASSACESI, *J. Chem. Phys.* **70**, 2834 (1979).
20. D. M. I. GOODGAME AND G. BRUN, *Bull. Soc. Chim. Fr.* **7**, 2236 (1973).
21. S. MISUMI, T. ISOBE, AND K. SUGIYAMA, *Bull. Chem. Soc. Jpn.* **47**, 1 (1974).
22. J. R. WASSON, D. M. KLASSEN, H. W. RICHARDSON, AND W. E. HATFIELD, *Inorg. Chem.* **16**, 1906 (1977).
23. A. BENCINI AND D. GATTESCHI, *Inorg. Chem.* **16**, 1994 (1977).
24. A. BENCINI, I. BERTINI, D. GATTESCHI, AND A. SCOZZAFAVA, *Inorg. Chem.* **17**, 3194 (1978).
25. L. D. ROLLMAN AND S. I. CHAN, *J. Chem. Phys.* **50**, 3416 (1969).
26. J. C. CONESA AND J. SORIA, *J. Magn. Reson.* **33**, 295 (1979).
27. S. S. ROMDHANE, G. BACQUET, AND G. BONEL, *J. Solid State Chem.* **40**, 34 (1981).