Computer Programs. The ANUCRYS structure determination package[13,14] was used for all aspects of the crystal structure analysis.

Registry No. (*R,S*)-**1**, 80127-37-3; (*R*)-**1**, 80183-96-6; (*S*)-**1**, 80183-97-7; (*R,S*)-**2**, 80127-38-4; (*R*)-**2**, 80183-98-8; (*S*)-**2**, 80183-99-9; (*R*)-**3**, 80145-77-3; (*R,R*)-**4**, 80226-02-4; (*R,S*)-**4**, 80145-79-5;

(*R,R*)-**5**, 80226-04-6; (*R,S*)-**5**, 80145-81-9; (*R*)-**6**, 80145-82-0; (*S*)-**6**, 80225-16-7; (*R*)-**7**, 80146-04-9; (*R,RR*)-**8**, 80160-35-6; (*R,SS*)-**8**, 80286-60-8; (*R,RR*)-**9**, 80146-06-1; (*R,SS*)-**9**, 80286-62-0; methylphenylphosphine, 6372-48-1; 8-chloroquinoline, 611-33-6; PhMeAsH, 53979-86-5.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table V), calculated hydrogen atom parameters (Table VI), and observed and calculated structure factor amplitudes (Table VII) (12 pages). Ordering information is given on any current masthead page.

(13) McLaughlin, G. M.; Taylor, D.; Whimp, P. O. "The ANUCRYS Structure Determination Package"; Research School of Chemistry, The Australian National University: Canberra, A.C.T., Australia 2600.
(14) Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* **1979,** *101,* 2363.

Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Synthesis and Characterization of Sterically Hindered CuN₄ Complexes of Tripod Ligands[1]

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The synthesis of tris[2-(1-pyrazolyl)ethyl]amine (trpyn) and its 3,5-dimethylpyrazolyl and 3,5-di-*tert*-butylpyrazolyl derivatives is described. The ligands form trigonal-pyramidal Cu(I) and square-pyramidal Cu(II) complexes, which show unusual electrochemistry as a result of pronounced environmental effects. The $E_{1/2}$ values for the three Cu(I) complexes are 0.49, 0.67, and 0.94 V vs. SCE, respectively. The last is the highest potential ever recorded for a CuN₄ complex and results because the alkyl groups on the pyrazole rings form a nonpolar pocket, protecting the copper atom from approach of the solvent or a counterion that would stabilize the 2+ valence. The compounds reported here also represent the first structurally characterized copper complexes of tripod ligands having three-atom bridges between ligating termini. Crystal data for [Cu(trpyn)H₂O][BF₄]₂: triclinic, $a = 9.9673$ (57) Å, $b = 12.9565$ (28) Å, $c = 9.4734$ (33) Å, $\alpha = 91.2446$ (258)°, $\beta = 103.4556$ (422)°, $\gamma = 106.7023$ (261)°, $V = 1134.36$ Å³, space group $P\bar{1}$, $Z = 2$. Crystal data for [Cu(trpynMe₆)]BF₄: orthorhombic, $a = 16.904$ (8) Å, $b = 16.985$ (6) Å, $c = 17.407$ (16) Å, $V = 4997.87$ Å³, space group $Pbca$, $Z = 8$.

Interest in modeling "blue-copper" proteins has focused mainly on their unusual spectroscopic and structural properties.[2] Of fundamental importance, however, is the ability of those proteins to shuttle electrons in biological systems at essentially diffusion-controlled rates.[3] The distorted geometry of the active site,[4] which also apparently governs the EPR and near-IR spectral parameters,[5] is thought to play a key role in the electron transfer since no molecular reorganization is required during the redox process.[6] The high reduction potential for blue-copper proteins[7] is another puzzling feature which has been difficult to explain; however, it is generally accepted that the nonplanar geometry of the copper ion or the nature of the ligands bound to copper is important in that regard.[7,8]

In this paper we describe the synthesis and characterization of a series of copper complexes of ligands **1–3** which display very high reduction potentials due to pronounced environmental effects. The compounds reported here also represent the first structurally characterized copper complexes of tripod

ligands having three-atom bridges between ligating termini.
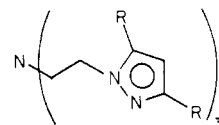
1, R = H (trpyn)
2, R = CH₃ (trpynMe₆)
3, R = *t*-C₄H₉ (trpynBu₆)

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. The following solvents were distilled: *N,N*-dimethylformamide (DMF), from sodium hydride under reduced pressure; tetrahydrofuran (THF), from sodium–benzophenone ketyl under nitrogen; methanol, from Mg(OCH₃)₂ under nitrogen. 3,5-Dimethylpyrazole and 3,5-di-*tert*-butylpyrazole were prepared by literature methods.[9] Melting points were obtained with use of a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, NC, and by Galbraith Laboratories, Inc., Knoxville, TN.

¹H NMR spectra were recorded on a Varian XL-100 instrument operating in the FT mode at 100.1 MHz. All chemical shifts are relative to an internal standard of Me₄Si. EPR spectra on samples frozen in a glass of 1:1 methanol–THF at 77 K were obtained with use of a Varian E-3 spectrometer, calibrated with DPPH. Electronic spectra were taken on a Cary 17 spectrophotometer.

Tris[2-(1-pyrazolyl)ethyl]amine (1). Under a nitrogen atmosphere, 6.7 g (0.1 mol) of pyrazole was added slowly to a suspension of 2.4 g (0.1 mol) of NaH in 130 mL of dry DMF. The solution was allowed to stir at 60 °C for 3 h, and then an additional 0.75 g of NaH was added. To the resulting suspension was added, in small portions, 6.03

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(2) (a) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979,** *101,* 4180–4192. (b) Downes, J. M.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1981,** *20,* 1081–1086.
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(5) Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980,** *102,* 168–178.
(6) McArdle, J. V.; Coyle, C. L.; Gray, H. B.; Yoneda, G. S.; Holwerda, R. A. *J. Am. Chem. Soc.* **1977,** *99,* 2483–2489 and reference therein.
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g (0.025 mol) of tris(2-chloroethyl)amine hydrochloride.[10] The mixture was allowed to stir vigorously for 36 h at 60 °C (large scale, 72 h) before the solvent was evaporated under reduced pressure. The residue was treated with 100 mL of water, and the solution was extracted with two 75-mL portions of benzene. The combined organic portions were washed with 50 mL each of water and saturated NaCl and dried over Na_2SO_4. The solvent was evaporated to give 7.75 g (100%) of a yellow oil. The product was further purified by bulb-to-bulb distillation at 190–200 °C (0.05 torr). ^1H NMR (CDCl₃): δ 2.88 (2 H, t, J = 6 Hz), 3.85 (2 H, t, J = 6 Hz), 6.14 (1 H, t, J = 2 Hz), 6.81 (1 H, d, J = 2 Hz), 7.50 (1 H, d, J = 2 Hz).

Tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (2). The same procedure as given above for **1** was followed. ^1H NMR (CD₃COCD₃): δ 2.13 (3 H, s), 2.22 (3 H, s), 2.91 (2 H, t, J = 7 Hz), 3.91 (2 H, t, J = 7 Hz), 5.76 (1 H, s).

Tris{2-[3,5-bis(2-methyl-2-propyl)-1-pyrazolyl]ethyl}amine (3). The same procedure as above gave a solid, which was crystallized from methanol–water: yield 68%; mp 124–125 °C. ^1H NMR (CD₃COCD₃): δ 1.24 (9 H, s), 1.39 (9 H, s), 3.16 (2 H, t, J = 7 Hz), 4.22 (2 H, t, J = 7 Hz), 5.87 (1 H, s). Anal. (C₃₉H₆₉N₇) C, H, N.

Aquo{[2-(1-pyrazolyl)ethyl]amino}copper(II) Bis(tetrafluoroborate), [Cu(trpyn)H₂O][BF₄]₂ (4). To a solution of 2.0 g (6.6 mmol) of **1** in 10 mL of methanol was added a solution of 2.3 g (6.6 mmol) of Cu(BF₄)₂·6H₂O in 15 mL of methanol. The resulting blue solution was gently heated for 10 min, and the solvent was evaporated to dryness under reduced pressure.[11] The residue was dissolved in 30 mL of 1:1 methanol–acetone and treated slowly with 40–50 mL of ethyl acetate. Large blue crystals formed upon standing overnight.[12] Anal. (C₁₅H₂₃B₂CuF₈N₇O) C, H, N.

Aquo{tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amino}copper(II) Bis(tetrafluoroborate), [Cu(trpynMe₆)H₂O][BF₄]₂ (5). A solution of 0.82 g (2.4 mmol) of Cu(BF₄)₂·6H₂O in 75 mL of CH₃CN was allowed to stand over 3-Å molecular sieves for 3 h before its addition to a stirred solution of 1.02 g (2.66 mmol) of **2** in 25 mL of CH₃CN. The resulting blue-green solution was evaporated to dryness under vacuum at 25 °C, and the residue was crystallized from CH₃CN–THF by slow evaporation of the solvent in air. Anal. Calcd for C₂₁H₃₅B₂CuF₈N₇O: C, 39.5; H, 5.52; N, 15.3. Found: C, 38.6; H, 5.45; N, 15.3.[13]

{Tris[2-(1-pyrazolyl)ethyl]amino}copper(I) Tetrafluoroborate, [Cu(trpyn)]BF₄ (6). In an inert-atmosphere box, 3.0 g (10 mmol) of **1** in 15 mL of CH₃CN was treated with a filtered solution of 3.2 g (10.6 mmol) of [Cu(CH₃CN)₄]BF₄ in 60 mL of CH₃CN. The resulting pale yellow solution was evaporated to dryness under vacuum and dissolved in 70 mL of methanol. Isopropyl alcohol was added, and the solution was allowed to stand for several days to give colorless crystals of **6**. It may also be crystallized from CH₃CN–THF. ^1H NMR (CD₃COCD₃): δ 3.12 (2 H, t, J = 4 Hz), 4.31 (2 H, t, J = 4 Hz), 6.39 (1 H, t, J = 2 Hz), 7.65 (1 H, d, J = 2 Hz), 7.84 (1 H, d, J = 2 Hz). Anal. (C₁₅H₂₁BCuF₄N₇) C, H, N.

{Tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amino}copper(I) tetrafluoroborate, [Cu(trpynMe₆)]BF₄ (7), was prepared as described for **6** and crystallized by slow evaporation of a methanol–isopropyl alcohol solution in inert atmosphere. ^1H NMR (CD₃COCD₃): δ 2.25 (3 H, s), 2.30 (3 H, s), 3.06 (2 H, t, J = 4 Hz), 4.06 (2 H, t, J = 4 Hz), 6.00 (1 H, s). Anal. Calcd for C₂₁H₃₃BCuF₄N₇: C, 47.2; H, 6.23; N, 18.4. Found: C, 45.9; H, 6.16; N, 17.9.

{Tris{2-[3,5-bis(2-methyl-2-propyl)-1-pyrazolyl]ethyl}amino}copper(I) tetrafluoroborate, [Cu(trpynBu₆)]BF₄ (8), was prepared as described for **6** and crystallized from THF–hexane. ^1H NMR (CD₃COCD₃): δ 1.24 (9 H, s), 1.39 (9 H, s), 3.05 (2 H, t, J = 4 Hz), 4.53 (2 H, t, J = 4 Hz), 6.22 (1 H, s). Anal. Calcd for C₃₉H₆₉BCuF₄N₇: C, 59.6; H, 8.84; N, 12.5. Found: C, 59.4; H, 8.82; N, 12.0.

Electrochemical Measurements. Cyclic voltammetry experiments were carried out in a single-cell compartment with a volume of ca. 5 mL, with use of a PAR Model 173 potentiostat and a Model 175

universal programmer. For display purposes, both a storage oscilloscope and a Hewlett-Packard 7015B X-Y recorder were used.

The experiments were conducted in an acetonitrile solution that was 0.1 M in (TBA)BF₄. The concentration of metal complex was 5×10^{-3} M. A saturated calomel electrode was used for the reference electrode, a platinum bead for the working electrode, and a platinum wire for the auxiliary electrode. Potentials are reported vs. SCE.

Results and Discussion

We, like others,[14] chose to utilize tripod ligands in an attempt to constrain cupric ion to a tetrahedral geometry since the original goal of this work was to prepare nonplanar Cu(II) complexes that would show reversible electrochemical behavior similar to that for the blue-copper proteins. Models suggested that the inclusion of three atoms between ligating termini would have the requisite "bite" to span tetrahedral coordination sites. This is in contrast to other systems in which the tripod arms contain only two bridging atoms.[14b,c] The latter usually bind in a trigonal-pyramidal fashion.

Pyrazole-containing tripod ligands were chosen because they are simply prepared and easily modified, and we subsequently synthesized a series of increasingly sterically hindered molecules. Although the compounds do not undergo electrochemically reversible reactions, they nevertheless do show unusual redox behavior.

(A) Synthesis and Spectroscopy. Tris[2-(1-pyrazolyl)-ethyl]amine (trpyn) and its 3,5-dimethyl and 3,5-di-*tert*-butyl derivatives were prepared in good yield by the route shown in eq 1. The colorless Cu(I) and blue-green Cu(II) complexes

$$ (1) $$
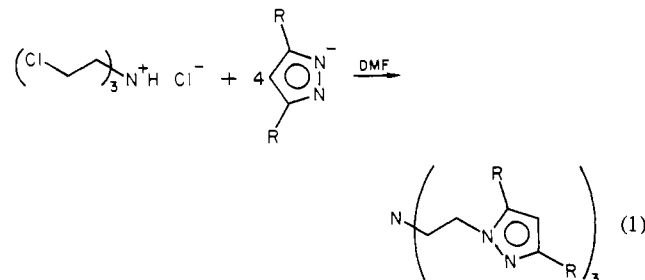
were readily synthesized from [Cu(CH₃CN)₄][BF₄] or Cu-(BF₄)₂·6H₂O in CH₃CN or methanol, respectively.[16] Although the Cu(I) complexes are not air-sensitive in the solid state or in CH₃CN, they were manipulated in an inert atmosphere. Attempts to prepare the Cu(II) complex of trpynBu₆ (3) were unsuccessful, and only the colorless Cu(I) derivative was obtained under all conditions.

Spectral data for the Cu(II) complexes are consistent with square-pyramidal geometry and may be taken as evidence that no gross geometrical change occurs in going from the solid state (vide infra) to solution. Electronic spectra show the following characteristics: for [Cu(trpyn)H₂O][BF₄]₂ (4) λ_{max} (nm) = 1007 (ϵ = 51 M^{-1} cm^{-1}) and 678 (89 M^{-1} cm^{-1}); for [Cu(trpynMe₆)H₂O][BF₄]₂ (5) λ_{max} (nm) = 800 (63 M^{-1} cm^{-1}) and 660 (61 M^{-1} cm^{-1}). The occurrence of two bands in the visible region is seen for other square-pyramidal complexes such as [Cu(trpn)NCS]$^+$ [17,18] and appears to be diag-

(10) Mason, J. P.; Gasch, D. J. *J. Am. Chem. Soc.* **1938**, *60*, 2816–2817. This compound is also commericaly available from Aldrich.

(11) All of the water must be evaporated or an oil will be obtained during crystallization.

(12) If one uses CuCl₂ instead of Cu(BF₄)₂ and then treats the resulting solution with NaBF₄, the complex [Cu(trpyn)Cl]BF₄ is obtained. EPR and electronic spectra show that this compound is also square pyramidal at copper.

(13) Calcd for [Cu(trpynMe₆)(H₂O)][BF₄]₂·¹/₂H₂O: C, 38.9; H, 5.60; N, 15.1.

(14) (a) Silvis, H. C.; Hendrix, D. C.; Averill, B. A., paper presented at the 178th National Meeting of the American Chemical Society, Sept Washington, D.C. 1979; see "Abstracts of Papers", INOR 203. (b) Karlin, K. D.; Dahlstrom, P. L.; Stanford, M. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1979**, 465–467. (c) Karlin, K. D.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Ibid.* **1980**, 906–908. (d) Mani, F. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 45–49.

(15) Bernarducci, E.; Schwindinger, W. F.; Hughey, J. L., IV; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1686–1691.

(16) Use of iron or cobalt salts also gave highly crystalline derivatives. These will be reported in due course.

(17) Abbreviations used in this paper which are otherwise undefined: trpn, tris(3-aminopropyl)amine; tren, tris(2-aminoethyl)amine; (TBA)BF₄, tetrabutylammonium tetrafluoroborate.
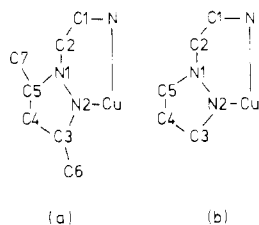
Figure 1. Numbering scheme for each arm of the tripod ligand in (a) [Cu(trpynMe$_6$)]BF$_4$ and (b) [Cu(trpyn)H$_2$O][BF$_4$]$_2$. Each arm is further identified by the letter a, b, or c as shown in Figures 2 and 3.
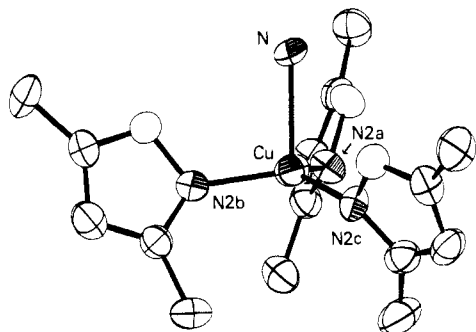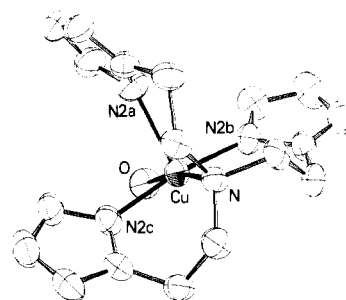

Figure 2. Molecular structure of [C(trpynMe$_6$)]$^+$. The ethylene bridges that connect the apical nitrogen with N1 of each pyrazole ring (shown as the open circle) have been omitted for clarity.

Table I. Interatomic Distances and Angles for [Cu(trpynMe$_6$)]BF$_4$

A. Bond Lengths, Å			
Cu–N	2.263 (4)	Cu–N2b	1.993 (4)
Cu–N2a	2.038 (4)	Cu–N2c	1.976 (4)

B. Nonbonding Intramolecular Contacts, Å			
C6a–C6b	4.133	C6a–C6c	4.124
C6b–C6c	4.064		

C. Bond Angles, Deg			
N–Cu–N2a	99.00 (18)	N2a–Cu–N2b	115.63 (18)
N–Cu–N2b	98.22 (17)	N2b–Cu–N2c	119.21 (17)
N–Cu–N2c	98.55 (18)	N2a–Cu–N2c	118.58 (17)

nostic for that geometry.[19] Similarly, EPR data show a better correlation with those for known square-pyramidal Cu(II) species ($g_\parallel > g_\perp > 2.00$; $A_\parallel = (120–150) \times 10^{-4}$ cm^{-1}) than for parameters exhibited by trigonal-bipyramidal Cu(II) complexes ($g_\perp > g_\parallel > 2.00$; $A_\parallel = (60–100) \times 10^{-4}$ cm^{-1}).[20] For **4**, $g_\parallel = 2.28$, $g_\perp = 2.09$, and $A_\parallel = 153 \times 10^{-4}$ cm^{-1} while for **5**, $g_\parallel = 2.23$, $g_\perp = 2.09$, and $A_\parallel = 156 \times 10^{-4}$ cm^{-1}. These data are curiously at odds with the results obtained for copper complexes of the analogous imidazole ligands, which are reported to be consistent with a distorted tetrahedral geometry.[14a]

The colorless and diamagnetic Cu(I) complexes were examined by NMR spectroscopy. NMR data for each cuprous complex, in conjunction with the structure of Cu(trpynMe$_6$)$^+$ (vide infra), suggest that they all have distorted trigonal-pyramidal geometries. The difference in chemical shift of the proton attached to C4 (see Figure 1 for the numbering scheme) between the free ligand and its Cu(I) derivative is 0.25 ppm for **1** and **6**, 0.24 ppm for **2** and **7**, and 0.35 ppm for **3** and **8**. We feel, therefore, that complexes **6** and **7** have essentially the same geometry, while complex **8** is distorted more toward a true trigonal pyramid. The interations of the *tert*-butyl groups attached to C3 in **8** will be more severe than those for the methyl groups in **7** (see Figure 2) and those interactions
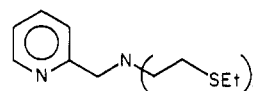

Figure 3. Molecular structure of [Cu(trpyn)H$_2$O]$^{2+}$.

will necessarily force the pyrazole rings upward.

(B) Molecular Structures.[21] **(1) [Cu(trpynMe$_6$)]BF$_4$ (7).** This complex crystallizes from CH$_3$CN–THF in the orthorhombic space group *Pbca*. Significant bond lengths and angles are complied in Table I, and final positional parameters are listed in Table II. The numbering scheme is shown in Figure 1a and the structure is presented in Figure 2.

The geometry of **7** can best be described as a distorted trigonal pyramid since the copper atom is only 0.298 Å above the plane formed by N2a, N2b, and N2c. In a tetrahedral complex, the copper would lie 0.667 Å above the plane, with the assumption of an average Cu–N distance of 2.0 Å. We originally thought that the C6 methyl groups, which create a pocket at the bottom of the molecule, were forcing the complex away from a tetrahedral geometry. However, the Me⋯Me interaction is >4.0 Å (see Table I), so it is doubtful that they have much effect, and the observed geometry is simply the most stable configuration that the ligand can adopt. In complex **8**, the *tert*-butyl groups probably do interact to distort the copper coordination sphere as mentioned above.

The Cu–N(amine) distance of 2.263 Å is somewhat longer than the Cu–N(amine) distance (2.158 Å) in Karlin's complex **(9)** formed between

(18) Vacca, A.; Paoletti, P. *J. Chem. Soc. A* **1968**, 2378–2383.

(19) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143–207.

(20) Bencini, A.; Bertini, I.; Gotteschi, D.; Scozzartara, A. *Inorg. Chem.* **1979**, *17*, 3194–3197.

(21) The crystal structures of **4** and **7** were determined by our colleague Professor D. J. Hodgson and his student Mr. Wayne Marsh at The University of North Carolina. Both structures were solved in essentially the same manner: a single crystal was mounted on the end of a glass fiber, and a preliminary diffractometer search revealed triclinic symmetry for **4** and orthorhombic for **7**. Systematic absences were observed for the latter consistent with the space group *Pbca*. Diffraction data were collected at 295 K on an Enraf-Nonius CAD-4 computer-controlled diffractometer using Mo Kα radiation from a graphite crystal monochromator. The unit cell constants were derived from a least-squares refinement of the setting angles of 25 reflections. The ω–2θ scan technique was used to record the intensities for all reflections for which $2° \leq \theta \leq 55°$. Peak counts were corrected for background to yield net intensities, I, which were assigned standard deviations calculated with a conventional p factor selected as 0.01. Intensities were corrected for Lorentz and polarization effects. A total of 4090 independent reflections had $I \geq 3\sigma(I)$ out of a total of 5197 reflections for **4**, and 1846 independent reflections had $I \geq 3\sigma(I)$ out of 4887 total reflections for **7**. Refinement of both structures was effected by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for nonhydrogen atoms were taken from ref 24 and those for hydrogen atoms from Stewart et al.[25] A three-dimensional Patterson synthesis was used to locate the metal atom, whose position phased the data sufficiently well to locate the other nonhyrogen atoms from difference Fourier maps. Crystal data for **4**: space group $P\bar{1}$, $Z = 2$, $a = 9.9673$ (57) Å, $b = 12.9565$ (28) Å, $c = 9.4734$ (33) Å, $\alpha = 91.2446$ (258)°, $\beta = 103.4556$ (422)°, $\gamma = 106.7023$ (261)°, $V = 1134.46$ Å^3. The final R factor (on F) was 0.0656. Crystal data for **7**: space group *Pbca*, $Z = 8$, $a = 16.904$ (8) Å, $b = 16.985$ (6) Å, $c = 17.407$ (16) Å, $\alpha = \beta = \gamma = 90.0°$, $V = 4997.87$ Å^3. The final R factor (on F) was 0.0590.

(22) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table II. Final Positional Parameters for [Cu(trpynMe₆)]BF₄

atom	x	y	z	atom	x	y	z
Cu	0.22641 (5)	0.00899 (5)	0.23916 (5)	B	−0.0144 (7)	0.2982 (6)	0.0423 (6)
F1	−0.0521 (4)	0.2572 (3)	0.0968 (3)	H1a1	0.2940 (0)	0.1825 (0)	0.0988 (0)
F2	0.0063 (4)	0.3683 (3)	0.0782 (4)	H1a2	0.2882 (0)	0.1974 (0)	0.1866 (0)
F3	−0.0604 (3)	0.3169 (3)	−0.0161 (3)	H1b1	0.4135 (0)	0.1308 (0)	0.1729 (0)
F4	0.0502 (4)	0.2637 (5)	0.0246 (4)	H1b2	0.4132 (0)	0.0415 (0)	0.1916 (0)
N	0.3059 (3)	0.0816 (3)	0.1623 (3)	H1c1	0.3592 (0)	0.0614 (0)	0.0579 (0)
N1a	0.1466 (3)	0.1585 (3)	0.2179 (3)	H1c2	0.2682 (0)	0.0500 (0)	0.0551 (0)
N2a	0.1399 (3)	0.0902 (3)	0.2588 (3)	H2a1	0.1654 (0)	0.1163 (0)	0.1126 (0)
N1b	0.3707 (3)	0.0378 (3)	0.3311 (3)	H2a2	0.1638 (0)	0.2077 (0)	0.1143 (0)
N2b	0.3021 (3)	−0.0081 (3)	0.3253 (3)	H2b1	0.3350 (0)	0.1420 (0)	0.2936 (0)
N1c	0.2435 (3)	−0.0872 (3)	0.1013 (3)	H2b2	0.4263 (0)	0.1357 (0)	0.3006 (0)
N2c	0.2042 (3)	−0.0784 (3)	0.1674 (3)	H2c1	0.3543 (0)	−0.0590 (0)	0.1409 (0)
				H2c2	0.3536 (0)	−0.0700 (0)	0.0525 (0)
C1a	0.2712 (4)	0.1609 (4)	0.1466 (4)	H4a	0.0647 (0)	0.2196 (0)	0.3672 (0)
C2a	0.1804 (5)	0.1605 (4)	0.1428 (4)	H4b	0.4076 (0)	−0.0951 (0)	0.4505 (0)
C3a	0.1055 (4)	0.1087 (4)	0.3248 (4)	H4c	0.0979 (0)	−0.1928 (0)	0.0626 (0)
C4a	0.0887 (4)	0.1892 (4)	0.3258 (4)	H6a1	0.0649 (0)	0.0683 (0)	0.4301 (0)
C5a	0.1154 (4)	0.2194 (4)	0.2585 (4)	H6a2	0.0553 (0)	0.0061 (0)	0.3655 (0)
C6a	0.0888 (5)	0.0472 (4)	0.3834 (4)	H6a3	0.1379 (0)	0.0215 (0)	0.4012 (0)
C7a	0.1177 (5)	0.3011 (4)	0.2282 (4)	H7a1	0.0950 (0)	0.3377 (0)	0.2640 (0)
C1b	0.3838 (4)	0.0903 (4)	0.1986 (4)	H7a2	0.1720 (0)	0.3180 (0)	0.2194 (0)
C2b	0.3770 (4)	0.1076 (4)	0.2837 (4)	H7a3	0.0903 (0)	0.3056 (0)	0.1807 (0)
C3b	0.3123 (4)	−0.0667 (4)	0.3754 (4)	H6b1	0.2661 (0)	−0.1675 (0)	0.4224 (0)
C4b	0.3856 (5)	−0.0599 (4)	0.4116 (4)	H6b2	0.2002 (0)	−0.1086 (0)	0.3987 (0)
C5b	0.4202 (4)	0.0070 (4)	0.3832 (4)	H6b3	0.2437 (0)	−0.1577 (0)	0.3365 (0)
C6b	0.2509 (5)	−0.1298 (4)	0.3822 (4)	H7b1	0.5287 (0)	0.0137 (0)	0.4371 (0)
C7b	0.4999 (5)	0.0439 (5)	0.3995 (5)	H7b2	0.5320 (0)	0.0457 (0)	0.3537 (0)
C1c	0.3150 (4)	0.0407 (4)	0.0874 (4)	H7b3	0.4941 (0)	0.0961 (0)	0.4183 (0)
C2c	0.3218 (4)	−0.0493 (4)	0.0953 (4)	H6c1	0.0314 (0)	−0.1597 (0)	0.2030 (0)
C3c	0.1356 (4)	−0.1205 (4)	0.1570 (4)	H6c2	0.0982 (0)	−0.1518 (0)	0.2635 (0)
C4c	0.1368 (5)	−0.1564 (4)	0.0855 (4)	H6c3	0.0559 (0)	−0.0771 (0)	0.2328 (0)
C5c	0.2073 (4)	−0.1340 (4)	0.0522 (4)	H7c1	0.2047 (0)	−0.1926 (0)	−0.0524 (0)
C6c	0.0761 (5)	−0.1268 (5)	0.2179 (5)	H7c2	0.2452 (0)	−0.1109 (0)	−0.0581 (0)
C7c	0.2396 (5)	−0.1539 (5)	−0.0239 (4)	H7c3	0.2902 (0)	−0.1813 (0)	−0.0220 (0)

Table III. Interatomic Distances and Angles for [Cu(trpyn)H₂O](BF₄)₂

A. Bond Lengths, Å

Cu–O	2.070 (2)	Cu–N2b	1.994 (2)
Cu–N	2.114 (2)	Cu–N2c	1.979 (2)
Cu–N2a	2.172 (2)		

B. Bond Angles, Deg

N–Cu–O	168.96 (7)	O–Cu–N2b	89.98 (8)
N–Cu–N2a	98.58 (8)	O–Cu–N2c	86.39 (8)
N–Cu–N2b	87.26 (8)	N2a–Cu–N2b	93.89 (9)
N–Cu–N2a	94.63 (8)	N2a–Cu–N2c	95.10 (9)
O–Cu–N2a	92.27 (8)	N2b–Cu–N2c	107.43 (9)

and Cu(I).[14c]

The difference is probably a result of the greater flexibility of our ligand, which permits the relatively "hard" amine nitrogen to be bound less tightly by the soft Cu(I) center. Having only two atoms between ligating termini as in **9** requires trigonal-pyramidal coordination and a shorter Cu–N-(amine) bond.

In all other respects, the structure is unexceptional, and bond distance and angles are in good agreement with those for other structures. There appear to be no intermolecular interactions in the solid state.

(2) [Cu(trpyn)(H₂O)][BF₄]₂ (4). This product crystallizes from methanol–acetone–ethyl acetate in the triclinic space group *P*1̄. Significant bond lengths and angles are compiled in Table III, and final positional parameters in Table IV. The numbering scheme is shown in Figure 1b, and the structure is presented in Figure 3.

The structure of **4** is unexceptional with regard to bond distances and angles; however, it constitutes the first structure of a Cu(II) complex of a tripod ligand having three-atom bridges between ligating termini. Noteworthy is the fact that the geometry about copper is square pyramidal, with the copper atom sitting 0.178 Å above the plane defined by N,
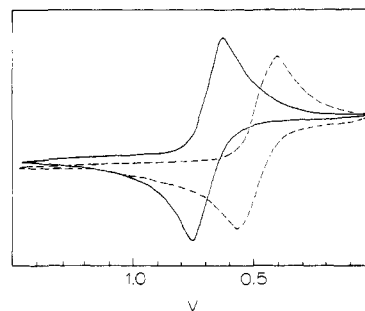

Figure 4. Cyclic voltammograms for **6** (---) and for **7** (—). Potentials are vs. SCE at a Pt electrode. The ordinate is an arbitrary scale of current.

O, N2b, and N2c. This in contrast with other complexes having tripod ligands, which are usually trigonal bipyramidal.[14c,24] For example, as mentioned above, complex **9** shows trigonal-pyramidal coordination in the Cu(I) state; but its oxidized form is five-coordinate trigonal bipyramidal with a sulfate ion coordinated axially to the copper.[14c] Thus, there is very little difference in the coordination of the ligand to the metal in the two oxidation states. Since the trpyn ligand is more flexible, it confers no geometrical constraints on the metal. This result thus serves to support the hypothesis that Cu(II) favors the square-pyramidal geometry over trigonal-bipyramidal coordination.[19] From the Cu(I) structure (vide supra), it is obvious that trpyn should be able to coordinate in the latter fashion.

(C) Electrochemistry. The results of cyclic voltammetric scans for **6** and **7** are shown in Figure 4. In acetonitrile with (TBA)BF₄[17] as the supporting electrolyte, both **6** and **7** un-

(24) See for example: Jain, P. D.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 6131–6136.

Table IV. Final Positional Parameters for $[Cu(trpyn)H_2O][BF_4]_2$

atom	x	y	z	atom	x	y	z
Cu	−0.13426 (6)	0.26586 (4)	0.18961 (6)	C1c	0.0495 (5)	0.2059 (4)	0.4595 (5)
F1	0.0081 (4)	0.7543 (3)	0.1693 (4)	C2c	0.1396 (5)	0.1910 (4)	0.3554 (6)
F2	0.0376 (9)	0.9251 (4)	0.2428 (5)	C3c	0.1469 (6)	0.4205 (4)	0.1608 (6)
F3	0.0785 (6)	0.8828 (4)	0.0323 (6)	C4c	0.2925 (6)	0.4345 (5)	0.1973 (6)
F4	−0.1259 (7)	0.8486 (6)	0.0593 (12)	C5c	0.3100 (5)	0.3506 (5)	0.2730 (6)
F5	0.4768 (6)	0.6801 (4)	0.4194 (6)	B1	0.0099 (7)	0.8577 (5)	0.1309 (7)
F6	0.6298 (6)	0.7942 (6)	0.3302 (7)	B2	0.5008 (7)	0.7504 (6)	0.3256 (9)
F7	0.4460 (10)	0.8200 (7)	0.3409 (12)	H1a	−0.2929 (0)	0.1984 (0)	0.4275 (0)
F8	0.4359 (10)	0.7181 (10)	0.1972 (8)	H1a'	−0.1750 (0)	0.1815 (0)	0.5696 (0)
O	−0.1627 (4)	0.3188 (3)	0.0167 (3)	H2a	−0.0294 (0)	0.3699 (0)	0.5491 (0)
				H2a'	−0.1705 (0)	0.3558 (0)	0.6150 (0)
N	−0.1084 (4)	0.1832 (3)	0.3793 (4)	H3a	−0.2129 (0)	0.5056 (0)	0.1179 (0)
N1a	−0.1946 (4)	0.4079 (3)	0.4147 (4)	H4a	−0.3337 (0)	0.5864 (0)	0.2823 (0)
N2a	−0.1619 (4)	0.4104 (3)	0.2840 (4)	H5a	−0.3037 (0)	0.4909 (0)	0.5209 (0)
N1b	−0.3847 (4)	0.0794 (3)	0.1705 (5)	H1b	−0.2271 (0)	0.0362 (0)	0.4272 (0)
N2b	−0.3443 (4)	0.1842 (3)	0.1450 (4)	H1b'	−0.0908 (0)	0.0291 (0)	0.3637 (0)
N1c	0.1809 (4)	0.2884 (3)	0.2803 (5)	H2b	−0.3222 (0)	−0.0552 (0)	0.1923 (0)
N2c	0.0758 (4)	0.3293 (3)	0.2092 (4)	H2b'	−0.2163 (0)	0.0409 (0)	0.1247 (0)
				H3b	−0.4712 (0)	0.2896 (0)	0.1000 (0)
C1a	−0.1867 (5)	0.2209 (4)	0.4778 (5)	H4b	−0.6851 (0)	0.1275 (0)	0.1293 (0)
C2a	−0.1379 (6)	0.3431 (4)	0.5258 (5)	H5b	−0.5824 (0)	−0.0338 (0)	0.1778 (0)
C3a	−0.2177 (6)	0.1847 (4)	0.2187 (6)	H1c	0.0600 (0)	0.1575 (0)	0.5409 (0)
C4a	−0.2829 (6)	0.5295 (4)	0.3063 (7)	H1c'	0.0897 (0)	0.2839 (0)	0.5062 (0)
C5a	−0.2675 (6)	0.4787 (4)	0.4317 (6)	H2c	0.0798 (0)	0.1273 (0)	0.2814 (0)
C1b	−0.1732 (6)	0.0628 (4)	0.3504 (6)	H2c'	0.2290 (0)	0.1737 (0)	0.4099 (0)
C2b	−0.2737 (6)	0.0253 (4)	0.2009 (6)	H3c	0.0985 (0)	0.4723 (0)	0.1072 (0)
C3b	−0.4659 (5)	0.2144 (4)	0.1233 (6)	H4c	0.3702 (0)	0.4951 (0)	0.1723 (0)
C4b	−0.5808 (6)	0.1272 (5)	0.1362 (7)	H5c	0.4071 (0)	0.3369 (0)	0.3207 (0)
C5b	−0.5279 (6)	0.0431 (5)	0.1644 (6)				

dergo chemically reversible oxidation–reduction reactions at high potentials at a platinum electrode ($E_{1/2}$ = +0.49 V and 0.69 V vs. SCE, respectively) with scan rates of 200 mV s^{-1}. Slower scan rates gave slightly smaller peak separations (100–120 mV), but the scans were never electrochemically reversible.

From the two reported structures it would appear that the quasi-reversibility for **6** and **7** is due to molecular reorganization when Cu(I) is oxidized to Cu(II) and vice versa. The high $E_{1/2}$ values for both **6** and **7** compared to those for other CuN$_4$ complexes[7] arise from the constrained nature of the ligand, which favors coordination to Cu(I) in order to minimize steric interactions. Since most other CuN$_4$ complexes are derived from macrocyclic ligands that are planar and therefore stabilize Cu(II), their $E_{1/2}$ values are usually <−0.5 V.[25] Complexes of the form CuL$_4$ (L = pyridine, imidazole, NH$_3$) have $E_{1/2}$ values at ∼0.3 V vs. SHE.[7] The highest potential previously reported for a CuN$_4$ appears to be ∼0.77 V vs. SHE for Cu(2,2'-biquinolyl)$_2$$^+$.[26,7] In that species, steric effects prevent formation of a planar Cu(II) complex and stabilize the Cu(I) form.

The higher potential for the methyl derivative **7** relative to **6** is due to "environment" effects. The pocket formed by the methyl groups on the bottom of the molecule (see Figure 2) is relatively nonplanar and therefore will hinder the approach of a polar solvent or charged counterion to the metal. Furthermore, the methyl substituents sterically prevent accessibility to copper. Thus, Cu(I) will be stabilized relative to Cu(II) since the former is already coordinatively saturated and solvation effects and the charge separation will be less pronounced.

Figure 5 shows the cyclic voltammetry results for compound **8**. In CH$_3$CN at a scan rate of 200 mV s^{-1}, **8** undergoes a one-electron oxidation followed by decomposition, and only a small reduction wave is observed. However, when the rate is increased to at least 5 V s^{-1}, a chemically reversible wave
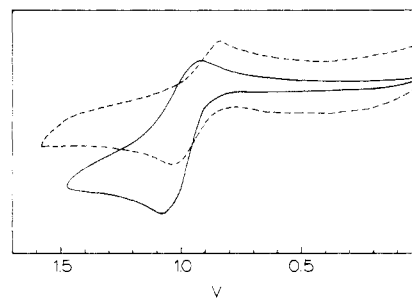

Figure 5. Cyclic voltammogram for **8** with scan rates of 200 mV s^{-1} (—) and of 5 V s^{-1} (- - -).

is seen, and $E_{1/2}$ for this process is +0.94 V vs. SCE at the platinum electrode. Molecular models show that a square-pyramidal complex cannot be formed with the *tert*-butyl-substituted ligand because of extreme steric hindrance. Therefore, stabilization of the Cu(II) state will be more difficult since the polar solvent or anion has to penetrate a sterically hindered hydrocarbon cavity on the bottom of the molecule (cf. Figure 2) in order to form a five-coordinate species. The reason for chemically irreversible behavior at the slower scan rates is probably due to oxidation at the tertiary nitrogen atom,[27] which distroys the complex.

Previously, workers in this field have questioned the "high" positive potential for blue-copper proteins relative to those for synthetic complexes. Geometrical perturbations[7] and sulfur coordination[8] are known to raise the potential of the Cu(I)–Cu(II) couple, and we now note that environmental effects also shift the potentials in a positive direction.[28] The $E_{1/2}$ of 0.94 V for **8** is the highest potential ever recorded, to our knowledge, for a CuN$_4$ complex. In light of these trends, it

(25) (a) Lindoy, L. F.; Tokel, N. E.; Anderson, L. B.; Busch, D. H. *J. Coord. Chem.* **1971**, *1*, 7–16. (b) Rillema, D. P.; Endicott, J. F.; Papconstantinou, E. *Inorg. Chem.* **1971**, *10*, 1739–1746.

(26) James, B. R.; Williams, J. P. *J. Chem. Soc.* **1961**, 2007–2019.

(27) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970; p 279.

(28) It is impossible to separate the steric from the hydrophobic effects in these complexes. Kassner[29] has estimated that hydrophobic effects can add up to 300 mV to the potential in heme complexes. If an effect of similar magnitude operates in our system, then steric effects must also be significant since $E_{1/2}$ for **8** is 450 mV more positive than $E_{1/2}$ for **6**.

(29) Kassner, R. J. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 2263–2267.

seems more reasonable to wonder why the potentials for the blue-copper systems are *so low* since X-ray crystallography of azurin[4b] and plastocyanin[4a] shows ligation of the copper by two sulfur atoms, extreme distortion from planar geometry, *and* the presence of an entirely hydrophobic environment about copper. Clearly, one difference is that our systems carry a greater overall charge in each oxidation state and that must contribute to a higher potential for our complexes based on electrostatic considerations. The statement that mercaptide sulfur produces a similar influence on the Cu(I)–Cu(II) potential as does a thioether sulfur[8] must be examined carefully therefore, since the anionic ligand will lower the overall charge on the complex and may accordingly shift the potential more negatively.

Registry No. **1**, 80049-12-3; **2**, 80049-13-4; **3**, 80049-14-5; **4**, 80062-90-4; **5**, 80062-92-6; **6**, 80083-21-2; **7**, 80063-16-7; **8**, 80063-18-9; [Cu(CH₃CN)₄]BF₄, 15418-29-8; 3,5-dimethylpyrazole, 67-51-6; 3,5-di-*tert*-butylpyrazole, 1132-14-5; pyrazole, 288-13-1; tris(2-chloroethyl)amine hydrochloride, 817-09-4.

Supplementary Material Available: Listings of observed and calculated structure factors and final positional and thermal parameters (50 pages). Ordering information is given on any current masthead page.

Mössbauer and X-ray Studies of Ferrous Malonate Dihydrate, Fe(C₃H₃O₄)₂·2H₂O

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Ferrous malonate dihydrate, Fe(C₃H₃O₄)₂·2H₂O, has been synthesized for the first time. The compound has a monomeric structure, isomorphous with magnesium malonate dihydrate with two molecules per unit cell and with space group $P2_1/c$ and unit cell dimensions $a = 4.96_1$ Å, $b = 11.40_3$ Å, $c = 9.61_6$ Å, and $\beta = 90.58°$. The temperature dependence of quadrupole splitting and optical spectral data give $\sim 10\,400$ cm⁻¹, ~ 700 cm⁻¹, ~ 100 cm⁻¹, and ~ 1200 cm⁻¹ for the 10*Dq*, tetragonal field, rhombic field, and splitting of the E_g level, respectively. The DTA and TGA curves indicate dehydration and decomposition to the oxide to occur at 160 and 350 °C, respectively.

Introduction

Previous studies on the organic acid salts of divalent iron limited to formate and oxalate showed that the monobasic acid salt has a structure quite different from that of the dibasic acid salt.[2] A dibasic acid higher up in the series such as malonic acid may be expected to give rise to an iron compound structurally different from that of formate and oxalate on account of the separation of the two carboxylic acid groups by a –CH₂– group reducing the spatial restriction in bonding. Our initial work on the malonate of iron employing Mössbauer spectroscopy provided evidence for the anticipated structural distinctions compared to those of formate and oxalate. As our own observations varied with those of Kwiatkowski et al.[3,4] on the iron malonic acid system, we have extended our work to an X-ray analysis of the powder pattern and established the isomorphous structure of the compound with magnesium malonate. As this system is being reported for the first time, information about the crystal field splitting of the ground state has been obtained by an analysis of the temperature dependence of quadrupole splitting.[5] Additional information on the crystal field splittings has been obtained by measuring the optical and photoacoustic spectra of the sample. The decomposition products of organic acid salts are of considerable interest.[6] Hence, DTA and TGA studies of the system have been carried out. The possible evidence for the existence of the anhydrous form is obtained by decomposing the hydrate absorber in the Mössbauer cryofurnace under vacuum. The results of our investigations by Mössbauer, X-ray diffraction, and optical spectral studies and DTA and TGA studies are presented in this paper.

Experimental Section

Ferrous malonate dihydrate was prepared by dissolving 500 mg of iron powder (electrolytic grade, Sarabhai Chemicals) in a hot aqueous solution containing an excess of malonic acid (Riedel) and concentrating the resultant solution to half the original volume and cooling to room temperature. Light green crystals separated out, which were filtered off on a Büchner funnel, washed with small quantities of water, and dried initially in air and then under vacuum at room temperature. Initially the preparations were carried out in a nitrogen atmosphere, but later it was found that the product is resistant to oxidation and can be conveniently prepared in the presence of air.

Physical Measurements. Microanalyses of carbon and hydrogen were carried out with use of a Hewlett-Packard Model 1858 C, H, N analyzer. Iron was analyzed by decomposing the product at 500 °C and weighing as Fe₂O₃. The analyses were found to correspond to the formula FeC₆H₁₀O₁₀. (Anal. Calcd: Fe, 18.74; C, 24.18; H, 3.38. Found: Fe, 18.54; C, 24.61; H, 3.52.) This suggested a molecular formula similar to that of magnesium malonate dihydrate, viz., Fe(C₃H₃O₄)₂·2H₂O.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out with use of a Mom-Budapest derivatograph employing a heating rate of 10 °C/min.

Mössbauer spectra were recorded with use of a constant-acceleration Elscint drive in conjunction with a multichannel analyzer (Promeda). The data were acquired in 512 channels with a mirror-image spectrum simultaneously acquired. At least 10⁵ counts were acquired to maintain good counting statistics. Measurements close to liquid-helium temperature were carried out with use of a modified Stohr 29–105 helium cryostat.[7] High-temperature measurements were made under vacuum

(1) (a) University of Hyderabad. (b) Regional Research Laboratory.
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