

of copper atoms from adjacent structural dimers. Since N-H...X interactions normally lead to ferromagnetic exchange, the J' coupling is likely due to intradimer coupling or to the longer interdimer Br...Br contacts.

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Note Added in Proof. As noted in the paper, the local coordination geometries in $(3AP)_2Cu_2Cl_6$ and $(guaninium)_2Cu_2Cl_6$ ^{19,40} are very similar. Indeed, the gross molecular geometries are nearly identical. Yet the 3AP salt is ferromagnetic ($J/k \approx 30$ K) while the latter is strongly antiferromagnetic ($J/k = -59$ K).⁴¹ It is worthwhile to determine whether there is a structural explanation and, indeed, if an intradimer source for the difference exists (in contrast to the new interdimer inter-

action in $(3AP)_2Cu_2Br_6 \cdot H_2O$). In reference to Figure 1, the pertinent distances and angles in the 3AP and guaninium salts are as follows: Cu-Cl(3), 2.496 vs 2.365 Å; Cl(2)-Cu-Cl(1a), 146.6 vs 134°; Cu-Cl(2), 2.320 vs 2.288 Å; Cu-Cl(2a), 2.330 vs 2.447 Å; Cu-Cl(2)-Cu, 119 vs 98°. While many features are similar, two important differences exist. The longer Cu-Cl bond has switched orientation, and thus the orientation of the magnetic orbitals will have changed. However, this factor may not be too significant since, for these geometries, the unpaired electrons will be in a strongly mixed combination of $d_{x^2-y^2}$ and d_{z^2} orbitals. Thus, the unpaired electron density at the bridging sites probably does not vary much for the two orientations. The more significant difference in this case would appear to be the bridging Cu-Cl-Cu angles, which are 3.1° larger for the guaninium complex than for the 3AP complex. A decrease in the value of J/k by 25-30 K per degree of angular variation is not unreasonable. Thus, this effect is clearly capable of accounting for the bulk of the observed variations in J .

Registry No. $[(C_5H_5N)NH_2]_2Cu_2Cl_6$, 112196-26-6; $[(C_5H_5N)NH_2]_2Cu_2Br_6 \cdot H_2O$, 112196-27-7.

Supplementary Material Available: Tables of thermal parameters and derived hydrogen positions (3 pages); listings of calculated and observed structure factors for both compounds (31 pages). Ordering information is given on any current masthead page.

- (40) Sundaralingam, M.; Carrabine, J. A. *J. Mol. Biol.* **1971**, *61*, 287. Declercq, J. P.; Debbaudt, M.; Van Meerssche, M. *Bull. Soc. Chim. Belg.* **1971**, *80*, 527.
- (41) Drake, D. F.; Crawford, V. H.; Laney, N. W.; Hatfield, W. E. *Inorg. Chem.* **1974**, *13*, 1246. Villa, J. F. *Inorg. Chem.* **1973**, *12*, 2054.

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2,2'-Bis(6-(2,2'-bipyridyl))biphenyl (TET), a Sterically Constricted Tetradentate Ligand: Structures and Properties of Its Complexes with Copper(I) and Copper(II)

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The synthesis of a new sterically constrained tetradentate N_4 ligand, 2,2'-bis(6-(2,2'-bipyridyl))biphenyl ($C_{32}H_{22}N_4 = TET$ (I)), is presented. Its Cu(I) and Cu(II) complexes have been prepared and characterized with the aid of crystal structure analyses, electrochemistry, and electronic spectroscopy. $[Cu^I(TET)]ClO_4 \cdot 2CH_3CN$ ($C_{32}H_{22}N_4Cu(ClO_4) \cdot 2C_2H_5N$) (II) crystallizes in the triclinic system ($P\bar{1}$) with $a = 10.585$ (2) Å, $b = 13.580$ (3) Å, $c = 14.025$ (2) Å, $\alpha = 61.18$ (1)°, $\beta = 84.67$ (1)°, $\gamma = 70.93$ (1)°, and $Z = 2$. The pseudotetrahedral cation $[Cu^I(TET)]^+$ shows a quasi-reversible Cu^I/Cu^{II} oxidation-reduction wave in the cyclic voltammogram at +0.94 V (NHE) in the noncoordinating solvent CH_2Cl_2 (counterion ClO_4^-) and has a strong metal-to-ligand charge-transfer absorption at 465 nm ($\epsilon = 4400$). In coordinating solvents (acetonitrile, tetramethylurea), the Cu^I/Cu^{II} potential drops, indicating coordinative changes upon oxidation. A stability constant $\log K$ of 6.9 (1) was determined for the reaction $TET + Cu^+ \rightleftharpoons [Cu(TET)]^+$ in acetonitrile. $[Cu^{II}(TET)Cl]ClO_4 \cdot CH_3CN$ ($C_{32}H_{22}N_4CuCl(ClO_4) \cdot C_2H_5N$) (III) crystallizes in the monoclinic system ($P2_1/c$) with $a = 12.860$ (2) Å, $b = 17.036$ (3) Å, $c = 14.585$ (2) Å, $\alpha = \gamma = 90^\circ$, $\beta = 96.33$ (2)°, and $Z = 4$. The cation $[Cu^{II}(TET)Cl]^+$ is five-coordinate, showing a distorted trigonal-bipyramidal arrangement of the donor atoms. Cl^- occupies an equatorial position.

Introduction

There is currently considerable interest in the synthesis of new ligands whose structure is such as to define quite precisely the stereochemistry of their complexation to a metal ion. In particular, in the chemistry of copper, which shows a variety of coordination geometries in both the +I and the +II oxidation state, the properties of the central ion are largely controlled via the imposed coordination environment. Diimine ligands, such as 2,2'-bipyridyl or 1,10-phenanthroline and substituted derivatives thereof, are known to enhance the stability of the Cu(I) oxidation state relative to Cu(II),¹ especially when tetrahedral coordination is favored by the presence of bulky substituents, as in the cases of the 2,9-disubstituted 1,10-phenanthrolines² or the 6,6'-disubstituted bipyridines,³ or by use of *catenand* type ligands.⁴ Another approach, recently reported for some Ni(II) compounds, is to vary the distance between two bidentate subunits within a N_4 macrocycle until strain effects in the bridges favor the adoption of a tetrahedral over the more usual planar structure. Lippard and co-workers⁵ showed two aliphatic bridges of six CH_2 groups between two diimine subunits to be an optimal choice in order to achieve a tetrahedral environment. In the case of the corresponding Cu(II)

complexes, however, the 6,6 system was too flexible, and only a dinuclear species could be obtained.⁶

Our new approach, the open-chain ligand 2,2'-bis(6-(2,2'-bipyridyl))biphenyl (TET (I)), is also based upon a bridge of six carbon atoms joining two diimine subunits. In order to limit flexibility, all atoms of the ligand are parts of aromatic six-membered rings. Through intramolecular rotations around the single bonds joining the aromatic rings, the ligand may readily provide a pseudotetrahedral coordination geometry, but in no case a square-planar one. The use of twisted biphenyl "spacers" has recently been reported for a CuN_2S_2 chromophore⁷ and for a CuN_4

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- (1) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.
 (2) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P.; Kirchoff, J. R.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1983**, 513.
 (3) (a) Burke, P. J.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1980**, *19*, 1211. (b) Burke, P. J.; Henrick, K.; McMillin, D. R. *Inorg. Chem.* **1982**, *21*, 1881.
 (4) Albrecht-Gary, A.-M.; Saad, Z.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1985**, *107*, 3205.
 (5) Davis, W. M.; Roberts, M. M.; Zask, A.; Nakanishi, K.; Nozoe, T.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 3864.
 (6) (a) Davis, W. M.; Zask, A.; Nakanishi, K.; Lippard, S. J. *Inorg. Chem.* **1985**, *24*, 3737. (b) Davis, W. M.; Lippard, S. J. *Inorg. Chem.* **1985**, *24*, 3688.
 (7) Anderson, O. P.; Becher, J.; Frydendahl, H.; Taylor, L. F.; Toftlund, H. *J. Chem. Soc., Chem. Commun.* **1986**, 699.

chromophore (during the preparation of this paper).⁸ In both cases, pseudotetrahedral Cu(II) complexes were obtained.

Experimental Section

Solvents and starting materials were purchased from Fluka. Benzene and tetramethylethylenediamine (TMED) were distilled under nitrogen from a NaH suspension. ZnCl₂ was sublimed in vacuo. [Ni(dppe)Cl₂] (dppe = 1,2-bis(diphenylphosphino)ethane),⁹ 2,2'-dilithiobiphenyl,¹⁰ and 6-chloro-2,2'-bipyridyl¹¹ were prepared according to literature methods. 6,6'-Dimethyl-2,2'-bipyridyl (dmbp) was prepared from commercial 2-amino-6-methylpyridine, by the method of Vogel for 2,2'-bipyridine.¹² In the meantime, a more efficient synthesis of dmbp has been published.¹³ For the preparation of 2,2'-dilithiobiphenyl, the slow procedure given by Schleyer et al.¹⁰ (3 days at ambient temperature) had to be employed, as the rapid procedure given by the same authors did not work in our hands for unknown reasons. The crystals of 2,2'-dilithiobiphenyl-bis(tetramethylethylenediamine) are readily soluble in benzene; this solution is stable at ambient temperature for a long time, in contrast to solutions in ether, which can only be kept for a short time, and in tetrahydrofuran, where the lithium reagent decomposes immediately at room temperature.

Preparation of 2,2'-Bis(6-(2,2'-bipyridyl)biphenyl) (TET (I)) (Scheme I). All manipulations were performed under N₂ by using Schlenk techniques. In a 200-mL Schlenk tube was dissolved 0.76 g (5.57 mmol) of anhydrous ZnCl₂ in 20 mL of boiling benzene containing 2.59 g (22.3 mmol) of TMED. Upon cooling, the zinc complex partly crystallized as a white solid. To this reaction mixture was added a solution of 2.22 g (5.57 mmol) of 2,2'-dilithiobiphenyl-bis(tetramethylethylenediamine) in benzene via a syringe at ambient temperature under stirring. The yellow color of the lithium reagent disappeared upon formation of the organozinc compound, and LiCl precipitated from the reaction mixture. The stoichiometric end point was indicated by persistence of a pale yellow color.

To the organozinc reagent was added a solution of 2.12 g (11.14 mmol) of 6-chloro-2,2'-bipyridine and 0.12 g (0.23 mmol) of red [Ni(dppe)Cl₂] as a catalyst in 50 mL of benzene. The reaction mixture, which turned olive green, was refluxed for 24 h, whereupon it became brown. Workup was done after cooling to ambient temperature by adding a solution of 2.4 g (6 mmol) of Na₂H₂EDTA and 5 mL of concentrated ammonia in 60 mL of water (in order to complex the Zn salts) and extracting the organic material with 4 × 60 mL of CH₂Cl₂.

The combined organic fractions were evaporated to dryness and digested with several portions of boiling *n*-heptane (in total about 300 mL) in order to extract the ligand. The combined extracts were decolorized with charcoal, filtered, and evaporated to a volume of about 30 mL. The ligand crystallized upon addition of 30 mL of *n*-pentane and storing at -20 °C for 1 day. Fine white needles of mp 172–174 °C were obtained. Yield: 460 mg (0.995 mmol; 18%).

The product was characterized by its mass spectrum (M⁺ *m/z* 462 (94%), decay peaks at *m/z* 461 (100%), 384 (7%), 307 (83%), 230 (23%), 155 (15%), and 78 (13%)) and its IR spectrum as well as its 60-MHz ¹H and its 50-MHz ¹³C NMR spectra; in the latter, 16 signals at 157.6, 156.2, 154.9, 148.6, 141.2, 139.6, 136.5, 136.4, 131.6, 129.8, 128.4, 127.2, 123.7, 123.3, 121.3, and 118.1 ppm (relative to TMS) were found (CDCl₃ solution). The UV/vis spectrum (CH₃CN solution) showed a π-π*-transition at 287 nm (ε = 34 000).

Preparation of [Cu^I(TET)]ClO₄·2CH₃CN (II). A solution of 231 mg (0.5 mmol) of TET (I) in 3 mL of CH₂Cl₂ was added to a solution of 163.5 mg (0.5 mmol) of [Cu^I(AN)₄]ClO₄ (prepared by reduction of Cu(ClO₄)₂·6H₂O with copper powder in acetonitrile) in 7 mL of acetonitrile (AN). An intense, red-brown color developed instantaneously. Vacuum evaporation at ambient temperature led to a brown, microcrystalline powder, which was recrystallized by dissolving it in a few milliliters of CH₂Cl₂, adding 20 mL of ethanol, and slowly evaporating the CH₂Cl₂ under reduced pressure at room temperature. Yield: 210 mg (80%).

Suitable crystals for X-ray structure analysis were grown by dissolving 25 mg of the product in about 1 mL of hot acetonitrile on the water bath and slowly cooling down to room temperature. These red-brown crystals contained acetonitrile and were only stable in the presence of a trace of the solvent.

Caution! Perchlorate salts are potentially explosive and should be handled with the necessary precautions.¹⁴

The complex was characterized by X-ray crystallography, its UV/vis spectrum (discussed later), and its 50-MHz ¹³C NMR spectrum. In the latter, 16 signals were found at 158.7*, 151.5*, 150.8*, 148.0*, 139.9*, 139.7, 138.8, 138.1, 130.7, 128.8, 128.6, 127.5, 127.0, 126.2, 122.1, and 119.8 ppm relative to TMS (CDCl₃ solution). The starred signals have been assigned to the carbon atoms without hydrogen substituents by an APT pulse sequence.

Preparation of [Cu^{II}(TET)Cl]ClO₄·CH₃CN (III). To a solution of 24.5 mg (52 μmol) of I in 10 mL of CH₂Cl₂ was added 10 mL of ethanol containing 26 μmol of Cu(ClO₄)₂·6H₂O and 26 μmol of CuCl₂·2H₂O. The resulting green solution was carefully evaporated on a rotary evaporator and the product recrystallized from 3 mL of hot acetonitrile as described above. Upon cooling, well-developed green crystals, suitable for X-ray work, were obtained. This product also contained acetonitrile, but the crystals were stable in air at ambient temperature.

The compound was characterized by X-ray crystallography, its IR spectrum, and its UV/vis spectra in solution and in the solid state. In solution, a d-d band at 764 nm (ε = 180) and a ligand-to-metal charge transfer at about 400 nm (ε = 400, shoulder at the low-energy side of the π-π* ligand absorptions) are visible. In the solid state (BaSO₄ dilution), a very broad d-d absorption band with two flat maxima at 850 and 1140 nm is seen.

Preparation of [Cu^{II}(TET)](ClO₄)₂·CH₃CN·H₂O. A solution of 24.5 mg (52 mmol) of I in 5 mL of acetonitrile was added to a solution of Cu(ClO₄)₂·6H₂O in 5 mL of acetonitrile. Filtration and concentration of the resulting green solution yielded, after addition of a few milliliters of ether and standing overnight, green crystals. Anal. Calcd for C₃₂H₂₅N₅O₉Cl₂Cu: C, 50.20; H, 3.32; N, 9.24. Found: C, 51.54; H, 3.65; N, 9.19.

Electronic Spectra. Solution spectra were measured on a Perkin-Elmer Lambda 5 spectrophotometer; diffuse reflectance spectra of the solid samples were obtained on a Perkin-Elmer 330 spectrophotometer equipped with an integrating sphere.

Electrochemical Measurements. Cyclic voltammograms were recorded by using a Tacussel PRGE-DEC potentiostat, connected to a function generator and an XY plotter. A three-electrode system, consisting of a glassy-carbon working electrode, a platinum counter electrode, and a nonaqueous Ag/Ag⁺ reference electrode, was used. Tetrabutylammonium perchlorate (TBAP) (0.1 M) served as an inert electrolyte in the three solvents acetonitrile (AN), tetramethylurea (TMU), and CH₂Cl₂. The reference potential was standardized against the known [Ru(bpy)₃](ClO₄)₂ system.¹⁵ The scan speed used was 0.2 V/s. The voltammograms were analyzed according to established procedures.¹⁵ The peak separation *E*_{pa} - *E*_{pc} of the voltammograms did not decrease upon slowing the scan speed to 0.1 V/s, indicating that voltage drops due to *iR* components were negligible under the specified conditions.

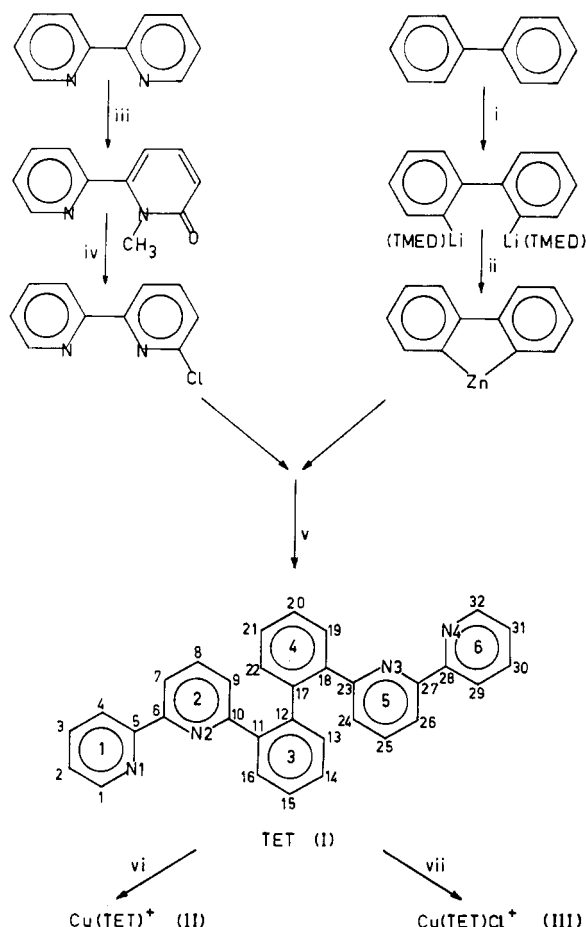
Determination of Stability Constants. Approximate values of the stability constants for the complexes of Cu⁺ with 2,2'-bipyridyl (bpy), 6,6'-dimethyl-2,2'-bipyridyl (dmbp), and TET were obtained from titrations of 20 mL of a 10⁻³ M solution of the corresponding ligand with a 5 × 10⁻³ M solution of Cu⁺ in acetonitrile (AN). The concentration of free Cu⁺ ion was monitored by the aid of a copper electrode immersed into the reaction mixture, against a nonaqueous Ag/Ag⁺ reference electrode. TBAP (0.1 M) was used as a supporting electrolyte. The copper electrode was standardized against known concentrations of Cu⁺. The influence of Cu²⁺ was minimized by carrying out all titrations under N₂, and 5 drops of a 0.1 M solution of N₂H₄·H₂O in AN were added to the solutions immediately before the titrations in order to maintain reducing conditions.¹⁶ Measurements were carried out at 20 °C.

Crystal Structures. Experimental data and structure refinement are summarized in Table I. The atom numbering of the ligand is shown in Scheme I. Diffracted intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation, ω/2θ scans, Lorentz and polarization corrections, and no absorption correction; structures were solved with MULTAN 80.¹⁷ Atomic scattering factors and anomalous dispersion terms were from ref 18, there

- (8) Knapp, S.; Keenan, T. P.; Zhang, X.; Fikar, R.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 1882.
 (9) Booth, G.; Chatt, J. J. *J. Chem. Soc.* **1965**, 3238.
 (10) Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107.
 (11) Case, F. H. *J. Org. Chem.* **1966**, *31*, 2398.
 (12) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed.; Longman: London, 1972; p 992.
 (13) Rode, Th.; Breitmaier, E. *Synthesis* **1987**, 574.

- (14) Raymond, K. N. *Chem. Eng. News* **1983**, *61* (Dec 5), 4. Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335; *Chem. Eng. News* **1963**, *41* (July 8), 47.
 (15) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980; Chapter 6.
 (16) Ayranci, J.; Daul, C.; Zobrist, M.; von Zelewsky, A. *Helv. Chim. Acta* **1975**, *58*, 1732.
 (17) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. "MULTAN80, a System of Computer Programs for the Automated Solution of Crystal Structures from X-ray Diffraction Data", Universities of York, England, and Louvain-la-Neuve, Belgium, 1980.

Scheme I. Synthesis of 2,2'-Bis(6-(2,2'-bipyridyl))biphenyl (TET)



^a (i) *n*-BuLi/hexane/TMED, room temperature, 3 days; (ii) ZnCl₂/TMED/C₆H₆; (iii) (a) CH₃I or (CH₃)₂SO₄, (b) K₃[Fe(CN)₆]/OH⁻; (iv) PCl₅/POCl₃, reflux; (v) [Ni(dppe)Cl₂] catalyst; (vi) [Cu^I(AN)₄](ClO₄) in acetonitrile; (vii) Cu^{II}Cl(ClO₄). (TMED = *N,N,N',N'*-tetramethylethylenediamine; dppe = bis(diphenylphosphino)ethane.)

was no secondary extinction correction, and all calculations were performed with a local version of the XRAY76¹⁹ and ORTEP II²⁰ programs. Table II gives the positional parameters, and Table III, some relevant bond distances, bond angles, and torsional angles. For compound II, the atomic positions of the two acetonitrile molecules have been refined but the hydrogen atoms of their methyl groups have not been localized. In compound III, both acetonitrile (four atomic sites observed) and perchlorate anion are disordered. The latter shows two preferential orientations: one major (about 75%), where the four oxygen atoms are relatively well localized, and one minor (about 25%), for which only three oxygen atoms have been observed. These disorders are presumably responsible for the relatively high final *R* value.

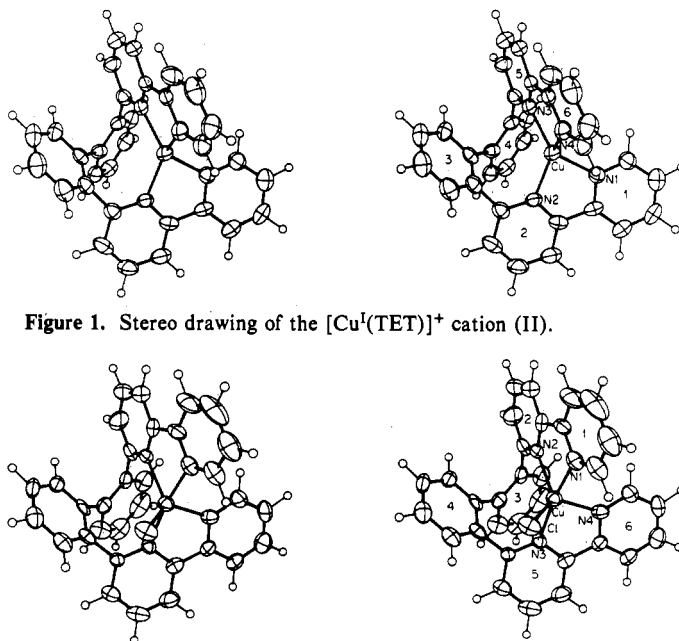
Results and Discussion

Ligand Synthesis. The method of synthesis of the TET ligand is shown in Scheme I. The key step consists of a cross coupling of an organometallic reagent with an aryl halide, catalyzed by a nickel phosphine complex (Felkin reaction).²¹ In our case, the direct use of 2,2'-dilithiobiphenyl as the organometallic component or the use of the corresponding transmetalated organomagnesium

Table I. Summary of Crystal Data, Intensity Measurement, and Structure Refinement

	II	III
formula	C ₃₂ H ₂₂ N ₄ Cu(ClO ₄)·2CH ₃ CN	C ₃₂ H ₂₂ N ₄ CuCl(ClO ₄)·CH ₃ CN
mol wt	707.7	702.1
cryst syst	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	10.585 (2)	12.860 (2)
<i>b</i> , Å	13.580 (3)	17.036 (3)
<i>c</i> , Å	14.025 (2)	14.585 (2)
α , deg	61.18 (1)	90
β , deg	84.67 (1)	96.33 (2)
γ , deg	70.93 (1)	90
<i>Z</i>	2	4
<i>D</i> _{calcd} , g cm ⁻³	1.412	1.468
<i>F</i> ₀₀₀	728	1436
μ , cm ⁻¹	7.840	9.029
cryst size, mm	0.12 × 0.20 × 0.35	0.18 × 0.20 × 0.31
unit cell determination	least-squares fit from 22 reflns (23° ≤ θ ≤ 33°)	least-squares fit from 20 reflns (21° ≤ θ ≤ 29°)
((<i>sin</i> θ)/ λ) _{max} , Å ⁻¹	0.505	0.481
no. of std reflns (variation)	2 (≤2.0%)	2 (≤1.0%)
no. of measd reflns	3522	3245
no. of unique reflns	3522	2952
criterion for obsd reflns	<i>F</i> ≥ 3 σ (<i>F</i>) and <i>F</i> ≥ 8	<i>F</i> ≥ 4 σ (<i>F</i>) and <i>F</i> ≥ 8
no. of observed reflections	2371	2163
refinement (on <i>F</i>)	four blocks	four blocks
no. of parameters	433	385
weighting scheme	$w(F) = \exp[18((\sin \theta)/\lambda)^2]$	$w(F) = (F /48)^2$ for <i>F</i> ≤ 48 $w(F) = (48/ F)^2$ for <i>F</i> ≥ 48
H atoms	calcd	calcd
max and av Δ/σ^2	6.86, 0.55	7.81, 0.37
max and min $\Delta\rho$, e Å ⁻³	0.55, -0.40	1.02, -1.00
<i>S</i>	5.74	4.60
<i>R</i> and <i>R</i> _w , %	4.7, 7.1	7.3, 6.6

^a The maximum values of Δ/σ are associated with the scale factor for II and with an oxygen atom of the disordered perchlorate for III.

Figure 1. Stereo drawing of the [Cu^I(TET)]⁺ cation (II).Figure 2. Stereo drawing of the [Cu^{II}(TET)Cl]⁺ cation (III).

analogue gave only traces of I. The organozinc reagent finally, in conjunction with [Ni(dppe)Cl₂] as the catalyst and benzene as the solvent, gave compound I in moderate yields. Addition of tetrahydrofuran (the solvent normally used in this type of coupling reactions) to the reaction mixture resulted in very poor yields of I. We believe this to be due to the presence of Li⁺ ions, which under the given conditions are able to activate ether linkages

- (18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.
- (19) Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. D. "The X-RAY76 System"; Technical Report TR-466; Computer Science Center, University of Maryland: College Park, MD, 1976.
- (20) Johnson, C. K. "ORTEP-II"; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
- (21) (a) Felkin, H.; Swiercwski, G. *Tetrahedron* **1975**, *31*, 2735. (b) Tamano, K.; Sumitani, K.; Kumuda, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.

Table II. Positional Parameters^a

	x	y	z		x	y	z	
(a) [Cu ^I (TET)]ClO ₄ ·2CH ₃ CN								
Cu ⁺	0.51426 (6)	0.32350 (5)	-0.14260 (5)	C15	0.7313 (5)	0.3227 (6)	0.1623 (5)	
Cl ⁻	0.25149 (16)	-0.04537 (12)	0.40922 (12)	PC	C16	0.6805 (5)	0.4110 (5)	0.0570 (5)
O1	0.2531 (6)	-0.1208 (5)	0.5234 (4)	PC	C17	0.8420 (4)	0.2510 (4)	-0.1054 (3)
O2	0.2784 (6)	0.0590 (5)	0.3900 (5)	PC	C18	0.8188 (4)	0.1575 (4)	-0.1107 (3)
O3	0.1263 (6)	-0.0108 (6)	0.3552 (5)	PC	C19	0.8742 (5)	0.1279 (4)	-0.1913 (4)
O4	0.3531 (6)	-0.1082 (5)	0.3653 (5)	PC	C20	0.9495 (5)	0.1888 (5)	-0.2653 (4)
N1	0.4418 (4)	0.4085 (4)	-0.3024 (3)		C21	0.9711 (5)	0.2824 (5)	-0.2631 (4)
N2	0.5764 (3)	0.4662 (3)	-0.1974 (3)		C22	0.9164 (4)	0.3139 (4)	-0.1824 (4)
N3	0.6080 (3)	0.1552 (3)	-0.0318 (3)		C23	0.7362 (4)	0.0911 (4)	-0.0313 (4)
N4	0.3583 (4)	0.2880 (4)	-0.0458 (3)		C24	0.7880 (5)	-0.0304 (4)	0.0421 (4)
C1	0.3713 (6)	0.3751 (5)	-0.3484 (4)		C25	0.7081 (6)	-0.0832 (4)	0.1179 (4)
C2	0.2987 (6)	0.4517 (6)	-0.4490 (5)		C26	0.5773 (5)	-0.0193 (4)	0.1212 (4)
C3	0.3038 (6)	0.5649 (5)	-0.5040 (4)		C27	0.5314 (4)	0.1011 (4)	0.0456 (3)
C4	0.3775 (5)	0.6009 (5)	-0.4597 (4)		C28	0.3932 (4)	0.1777 (4)	0.0404 (3)
C5	0.4459 (4)	0.5202 (4)	-0.3569 (4)		C29	0.3037 (6)	0.1405 (5)	0.1174 (4)
C6	0.5300 (4)	0.5498 (4)	-0.3016 (4)		C30	0.1745 (5)	0.2169 (6)	0.1040 (5)
C7	0.5578 (5)	0.6567 (5)	-0.3534 (5)		C31	0.1364 (5)	0.3271 (6)	0.0137 (5)
C8	0.6362 (6)	0.6778 (5)	-0.2964 (5)		C32	0.2307 (5)	0.3592 (5)	-0.0590 (5)
C9	0.6829 (5)	0.5944 (5)	-0.1903 (5)		C101	-0.0051 (7)	0.3378 (9)	0.3217 (9)
C10	0.6540 (4)	0.4861 (4)	-0.1429 (4)		C102	-0.0082 (10)	0.2371 (9)	0.4211 (9)
C11	0.7106 (4)	0.3901 (4)	-0.0328 (4)		N101	-0.0006 (11)	0.4116 (13)	0.2363 (13)
C12	0.7965 (4)	0.2787 (4)	-0.0142 (4)		C201	0.3171 (8)	0.0971 (9)	0.6178 (6)
C13	0.8465 (4)	0.1906 (5)	0.0917 (4)		C202	0.3956 (10)	-0.0256 (9)	0.6505 (8)
C14	0.8138 (5)	0.2131 (5)	0.1795 (4)		N201	0.2581 (9)	0.1934 (10)	0.5930 (7)
(b) [Cu ^{II} (TET)Cl]ClO ₄ ·CH ₃ CN								
Cu ²⁺	0.25068 (9)	0.55022 (8)	0.66791 (8)	C20	0.3679 (9)	0.3168 (7)	0.5049 (8)	
Cl ⁻ 1	0.28978 (19)	0.56234 (18)	0.51809 (17)	C21	0.3113 (8)	0.2725 (6)	0.5614 (9)	
N1	0.1066 (7)	0.5846 (6)	0.6241 (6)	C22	0.3090 (8)	0.2935 (6)	0.6525 (8)	
N2	0.1542 (5)	0.4583 (5)	0.7231 (5)	C23	0.4665 (7)	0.4802 (6)	0.6697 (6)	
N3	0.4062 (5)	0.5330 (4)	0.7060 (5)	C24	0.5727 (8)	0.4900 (7)	0.6707 (7)	
N4	0.2773 (6)	0.6342 (5)	0.7695 (5)	C25	0.6200 (8)	0.5554 (9)	0.7148 (8)	
C1	0.0889 (10)	0.6509 (8)	0.5779 (9)	C26	0.5593 (9)	0.6075 (7)	0.7557 (8)	
C2	-0.0087 (14)	0.6721 (9)	0.5324 (9)	C27	0.4513 (8)	0.5957 (6)	0.7506 (6)	
C3	-0.0861 (12)	0.6171 (14)	0.5359 (11)	C28	0.3796 (8)	0.6491 (6)	0.7932 (6)	
C4	-0.0705 (9)	0.5501 (10)	0.5850 (9)	C29	0.4126 (9)	0.7095 (7)	0.8552 (8)	
C5	0.0278 (8)	0.5329 (7)	0.6295 (7)	C30	0.3388 (11)	0.7521 (7)	0.8939 (9)	
C6	0.0553 (8)	0.4636 (6)	0.6855 (7)	C31	0.2350 (10)	0.7353 (7)	0.8699 (8)	
C7	-0.0221 (9)	0.4086 (9)	0.7040 (10)	C32	0.2070 (8)	0.6779 (7)	0.8085 (8)	
C8	0.0046 (12)	0.3491 (9)	0.7619 (13)	Cl ⁻ 2	0.9114 (3)	0.62893 (21)	0.8483 (3)	PC
C9	0.1050 (12)	0.3446 (7)	0.8081 (9)	O1*	0.9883 (12)	0.5669 (11)	0.8456 (11)	PC
C10	0.1784 (8)	0.4013 (6)	0.7859 (7)	O2*	0.9635 (11)	0.6983 (10)	0.8666 (11)	PC
C11	0.2852 (9)	0.3977 (6)	0.8352 (8)	O3*	0.8539 (12)	0.6558 (9)	0.7538 (11)	PC
C12	0.3711 (9)	0.3778 (6)	0.7896 (7)	O4*	0.8192 (12)	0.6079 (9)	0.8755 (11)	PC
C13	0.4707 (9)	0.3730 (7)	0.8408 (9)	O101*	0.945 (4)	0.562 (4)	0.816 (3)	PC
C14	0.4829 (12)	0.3920 (8)	0.9318 (10)	O102*	0.948 (4)	0.685 (3)	0.788 (3)	PC
C15	0.3981 (15)	0.4147 (8)	0.9756 (9)	O103*	0.916 (3)	0.640 (3)	0.937 (3)	PC
C16	0.3003 (12)	0.4169 (7)	0.9289 (9)	C101	0.7585 (15)	0.1587 (12)	0.3702 (14)	AN
C17	0.3613 (7)	0.3592 (7)	0.6894 (7)	C102	0.8055 (14)	0.1108 (12)	0.4133 (13)	AN
C18	0.4163 (7)	0.4072 (7)	0.6305 (7)	C103*	0.862 (3)	0.0817 (21)	0.4580 (24)	AN
C19	0.4213 (8)	0.3841 (7)	0.5406 (7)	C104*	0.729 (3)	0.1986 (22)	0.347 (3)	AN

^aStarred atoms are disordered; PC = perchlorate anion; AN = solvate acetonitrile.

toward nucleophilic attack by the organometallic reagent, which is thereby consumed in an unwanted side reaction.

Crystal Structures. Figures 1 and 2 show ORTEP drawings of the two cations [Cu(TET)]⁺ and [Cu(TET)Cl]⁺, respectively. Figure 3 shows a stereographic projection of the Cu–N bonds and the vectors Cu–P1 and Cu–P2, where P1 and P2 are the midpoints of the vectors N1–N2 and N3–N4.

The [Cu(TET)]⁺ cation shows a pseudotetrahedral coordination of Cu(I) with a mean Cu–N distance of 2.03 Å. The TET ligand adopts a noncrystallographic C₂ symmetry, as reflected by the dihedral angles between the individual aromatic rings. The dihedral "crossing" angle between the two bipyridyl subunits is 74.9°; this value, as well as the rest of the geometry, is comparable to those of other [M(diimine)₂]⁺ cations, where M⁺ is a d¹⁰ ion.^{2-4,22} Figure 3 shows that the angle P1–Cu–P2 is less (166°) than the expected value (180°) for ideal D_{2d} symmetry and that this appears to arise from the presence of the biphenyl spacer, the vectors

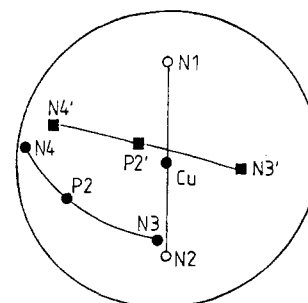


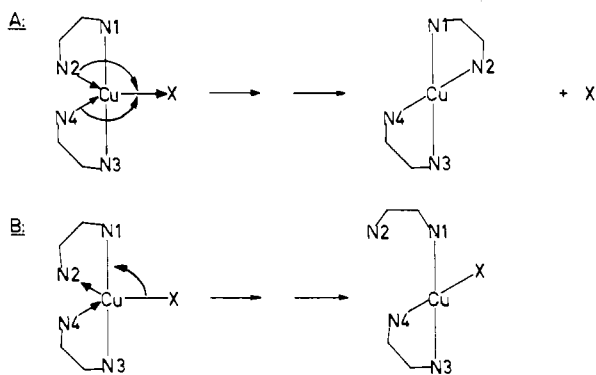
Figure 3. Stereographic projection of the Cu–N and the Cu–P2 vectors, viewed from Cu toward P1. N1 and N2 lie below the plane of the paper. N3', N4', and P2' are the positions for compound II; N3, P2, N4, those for compound III. The biphenyl bridge joins N2 and N3' or N3 and N4. P1 and P2 are the midpoints of the vectors N1–N2 and N3–N4.

Cu–P1 and Cu–P2 being displaced away from the bridge.

[Cu(TET)Cl]⁺ shows trigonal-bipyramidal coordination of the Cu(II) ion with a basal plane formed by Cl, N2, and N4. N1

Table III. Selected Geometric Parameters of the $[\text{Cu}^{\text{I}}(\text{TET})]^+$ and the $[\text{Cu}^{\text{II}}(\text{TET})\text{Cl}]^+$ Cations

	$[\text{Cu}^{\text{I}}(\text{TET})]^+$	$[\text{Cu}^{\text{II}}(\text{TET})\text{Cl}]^+$
Bond Lengths (Å)		
Cu-N1	2.047 (4)	1.981 (9)
Cu-N2	2.020 (4)	2.205 (8)
Cu-N3	2.001 (3)	2.037 (7)
Cu-N4	2.067 (4)	2.060 (8)
Cu-Cl		2.305 (5)
Bond Angles (deg)		
N1-Cu-N2	81.5 (2)	77.5 (3)
N1-Cu-N3	135.4 (2)	170.4 (4)
N1-Cu-N4	108.1 (2)	95.8 (3)
N2-Cu-N3	128.4 (2)	111.9 (3)
N2-Cu-N4	127.9 (2)	106.6 (3)
N3-Cu-N4	80.6 (1)	79.9 (3)
Cl-Cu-N1		87.8 (3)
Cl-Cu-N2		126.9 (2)
Cl-Cu-N3		87.8 (2)
Cl-Cu-N4		125.7 (2)
Dihedral Angles between Individual Aromatic Rings (deg)		
1-2	7.9	8.8
2-3	60.8	71.0
3-4	61.6	63.5
4-5	60.9	57.5
5-6	8.5	11.5

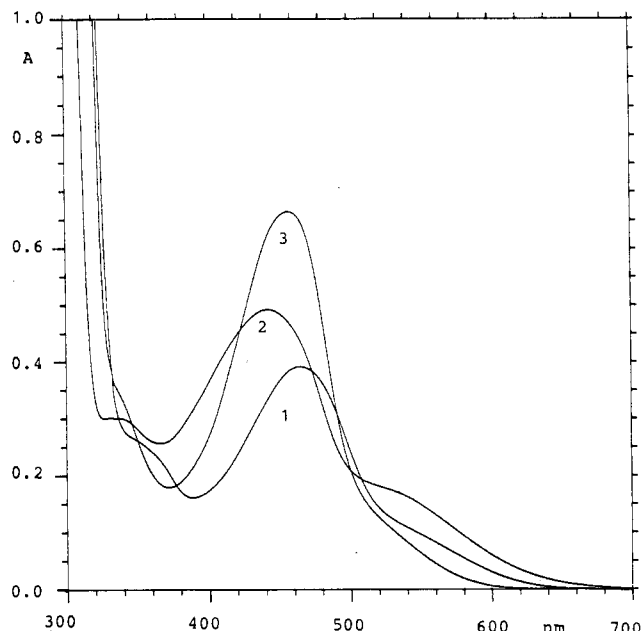
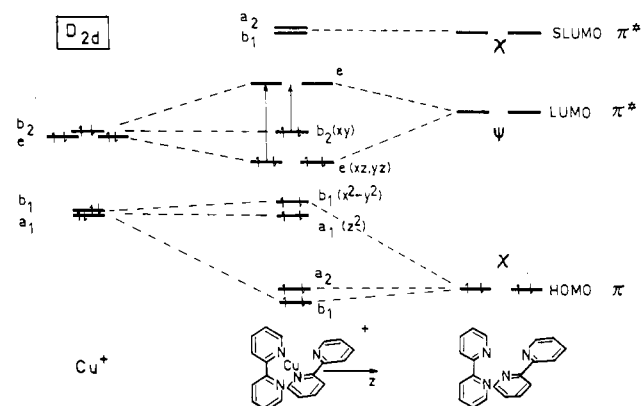
Scheme II. Main Deformation Modes A and B of the $[\text{Cu}^{\text{II}}(\text{diimine})_2\text{X}]^+$ Complexes

and N3 occupy the axial positions. The TET ligand is asymmetrically coordinated, one of its terminal nitrogen atoms being in an axial position (N1) and the other in an equatorial one (N4). In consequence, the copper ion lies 0.11 Å out of the basal plane, toward N3. The equatorial distance Cu-N2 (2.21 Å) is significantly longer than the remaining Cu-N distances (mean value 2.03 Å). Hathaway and co-workers discussed structural distortion pathways in analogous $[\text{Cu}^{\text{II}}(\text{bpy})_2\text{X}]$ chromophores^{23,24} and identified two major pathways of distortion from trigonal-bipyramidal (TBP) to square-planar or square-pyramidal (SP) complexes^{23,24} (Scheme II). In the totally symmetric pathway (A) the Cu-X bond elongates and the basal plane is formed by the four nitrogen atoms; in the antisymmetric pathway (B) one of the equatorial Cu-N bonds is lengthened, leading to an N_3X basal plane. A factor analysis of available crystallographic data confirms the existence of two major distortion coordinates.²⁵ Holmes has discussed the TBP-SP rearrangement and shown it to follow the

(23) Harrison, W. D.; Kennedy, D. M.; Power, M.; Sheahan, R.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1556.

(24) Hathaway, B. J. *Struct. Bonding (Berlin)* **1984**, 57, 55.

(25) Independently of Hathaway's work, we carried out a statistical factor analysis of 26 $[\text{Cu}(\text{L})_2\text{X}]$ complexes (L = bpy, phen) taken from the literature. The scatter plot of these structures in the 15-dimensional space of the chromophore's geometric parameters (5 bond lengths and 10 bond angles) lies essentially on a plane spanned by the eigenvectors of the trigonal-bipyramidal (A) and the equatorial asymmetric (B) deformations of the trigonal-bipyramidal CuN_4X chromophore, confirming Hathaway's results. The structures of such complexes may thus conveniently be discussed in terms of these two deformation parameters.

**Figure 4.** Charge-transfer spectra of (1) $[\text{Cu}(\text{TET})]\text{ClO}_4$, (2) $[\text{Cu}(\text{bpy})_2]\text{ClO}_4$, and (3) $[\text{Cu}(\text{dmbp})_2]\text{ClO}_4$, all 10^{-4} M in acetonitrile solution (bpy = 2,2'-bipyridyl; dmbp = 6,6'-dimethylbipyridyl).**Chart I.** MO Diagram for $[\text{Cu}^{\text{I}}(\text{diimine})_2]^+$ Chromophores

pathway expected for the Berry pseudorotation.²⁶ Although the bond angles in $[\text{Cu}(\text{TET})\text{Cl}]^+$ suggest that it lies close to the TBP extreme, the long Cu-N2 bond shows it to be an example of the B distortion pathway.

We believe this to be mainly a consequence of the steric strain induced by the biphenyl backbone of the ligand; the two corresponding $[\text{Cu}(\text{bpy})_2\text{Cl}]^+$ structures,²³ where no such strain is present, do not show such elongated equatorial Cu-N2 distances (2.14 and 2.11 Å, respectively). Examination of Figure 3 shows that the rearrangement of the TET ligand during the transition $\text{II} \rightarrow \text{III}$ involves primarily the displacement of atom N3. This can be achieved by slight changes of the torsion angles between the aromatic rings 2-3, 3-4, and 4-5 without involving other geometric parameters of the TET ligand (see Table III).

Stability Measurements. Titration experiments indicated a value of $\log K = 6.9$ (1) for the thermodynamic constant of the equilibrium $[\text{Cu}(\text{NCCH}_3)_4]^+ + \text{TET} \rightleftharpoons [\text{Cu}(\text{TET})]^+$ in acetonitrile. The corresponding $\log \beta_2$ values found by the same method for the complexes $[\text{Cu}(\text{dmbp})_2]^+$ and $[\text{Cu}(\text{bpy})_2]^+$ are 6.9 (1) and 4.8 (1), respectively. The enhanced stability of II with respect to the simple bpy complex results clearly from the tetradentate nature of the TET ligand. It is, however, smaller than one could expect; the stability of the TET complex is also reached with dmbp ligands. This could be an indication that some strain is induced

(26) Holmes, R. *J. Am. Chem. Soc.* **1984**, 106, 3745.

within the aromatic backbone of I upon its coordination to a metal ion, e.g. via a loss of conjugation energy between the crossed aromatic rings.

Electronic Spectra. In acetonitrile solution, $[\text{Cu}(\text{TET})]^+$ shows an intense absorption band at 465 nm ($\epsilon = 4400$) with a shoulder at 533 nm ($\epsilon = 1600$) and a feature at higher energy (347 nm, $\epsilon = 2800$). The spectrum is qualitatively very similar to those of $[\text{Cu}(\text{bpy})_2]^+$ and $[\text{Cu}(\text{dmbp})_2]^+$ (Figure 4). The main absorption at 465 nm is characteristic of a Cu(I)-diimine system and is generally attributed to a charge transfer from the filled metal d orbitals to the lowest empty π^* orbitals (LUMO) of the diimine (bipyridyl) ligands.²⁷ The origin of the observed three bands has not, to our knowledge, previously been discussed. If we assume pseudotetrahedral (D_{2d}) symmetry of the chromophore, then the highest metal d orbitals will be xz , yz (e), and xy (b_2), derived from the t_2 family of an ideal tetrahedron (Chart I). According to the calculations of Kaim et al.,²⁸ the lowest unoccupied π^* orbital (LUMO) of bipyridine (in free or in coordinated form) is of the Orgel ψ type,²⁹ followed by a second lowest unoccupied π^* orbital (SLUMO) about 1 eV above it, which is of the Orgel χ type.²⁹ Under the assumed D_{2d} symmetry, the combined ψ orbitals of the two bpy ligands transform as an e set, whereas the corresponding χ orbitals split into an a_2 and a b_1 representation.³⁰ The bpy LUMOs can thus strongly interact with the e orbitals arising from the Cu 3d shell and stabilize them, but they cannot react with b_2 , so that the lowest energy band in the absorption spectrum would correspond to a $b_2(xy) \rightarrow e(\pi^*)$ transition and the more intense main band to $e(xz, yz) \rightarrow e(\pi^*)$, both symmetry allowed. This would require a splitting between b_2 and e of some 2700 cm^{-1} . The shoulder at 347 nm can arise either from a transition from the lower lying d orbitals to the LUMOs (implying a ligand field splitting on the order of 8000 cm^{-1}) or from an excitation into high vacant π^* orbitals (SLUMOs) of the ligand. An analogous scheme has been given by McMillin et al.; these authors also discuss the influence of aryl substituents on the charge-transfer intensities in Cu(I) complexes with bipyridyl and phenanthroline ligands and show that these intensities decrease when the substituents are ortho to the coordinating nitrogen atoms.³¹ A similar effect is seen in the spectrum of $[\text{Cu}(\text{TET})]^+$ if compared to that of $[\text{Cu}(\text{bpy})_2]^+$: the biphenyl bridge in the former decreases the intensity of the main absorption band with respect to the unsubstituted "parent compound".

The spectra of the corresponding Cu(II) complexes show broad d-d absorption bands in the region 600–900 nm (acetonitrile solution). These bands are red-shifted in the solid state, as seen from the diffuse-reflectance spectra. The origin of these bands in analogous complexes has been discussed by Hathaway and coworkers.²⁴

Electrochemistry. Cyclic voltammetry studies on solutions of II showed a quasi-reversible one-electron oxidation-reduction wave associated with the Cu(I)/Cu(II) couple, whose position was strongly solvent dependent (Figure 5).

Values (with respect to the NHE) are as follows: +0.70 V in tetramethylurea (TMU), $E_{pc} - E_{pa} = 180 \text{ mV}$; +0.72 V in acetonitrile (AN), $E_{pc} - E_{pa} = 100 \text{ mV}$; +0.94 V in dichloromethane, $E_{pc} - E_{pa} = 80 \text{ mV}$. Two reversible ligand reduction waves at -1.34 and -1.61 V were also observed in all three solvents. The irreversibility of the observed Cu(I)/Cu(II) wave suggests that a rapid chemical reaction follows the electron-transfer step, i.e. that coordinative changes take place at the copper ion upon oxidation or reduction on the electrochemical time scale.

The difference between the reduction potential of the Cu^{2+} ion and the first reduction potential of the ligand in the TET complex may be compared with the orbital energy difference between HOMO and LUMO as measured by the metal-to-ligand

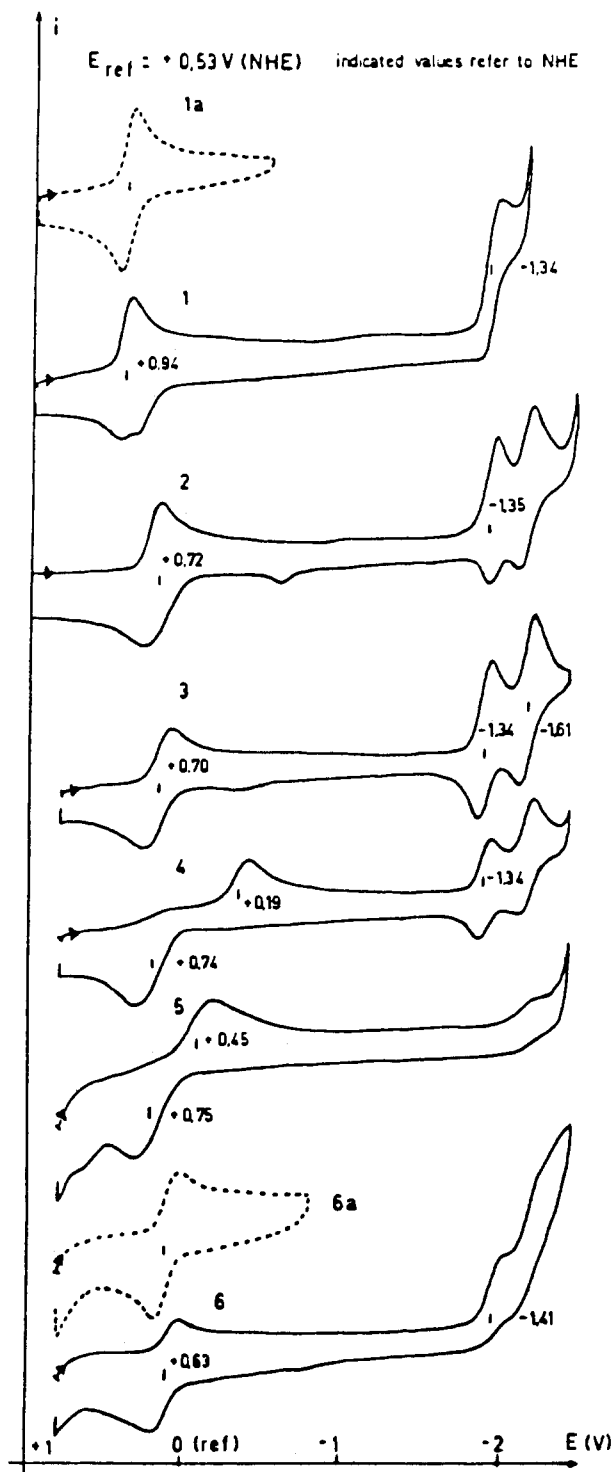


Figure 5. Cyclic voltammograms of (1) $[\text{Cu}(\text{TET})]\text{ClO}_4$ (II) in CH_2Cl_2 (curve 1a: only $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ wave scanned), (2) II in acetonitrile, (3) II in tetramethylurea (TMU), (4) II in TMU with 1 equiv of Cl^- (tetra-butylammonium chloride) added, (5) II in TMU with excess Cl^- (5 equiv) added, and (6) same solution as in (5) after addition of 10 vol % water (curve 6a: only $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ wave scanned). The scan directions are indicated by arrows.

charge-transfer absorption frequency³² of $[\text{Cu}^{\text{I}}(\text{TET})]^+$. In AN, this band is observed at 21500 cm^{-1} (2.66 eV), which is considerably greater than the reduction potential difference (ranging between 2.04 and 2.28 V in the various solvents investigated); this large discrepancy of 0.38–0.62 V is indicative of a system showing considerable inner-sphere rearrangements following the electro-

(27) Daul, C.; Schläpfer, C. W.; Goursot, A.; Pénigault, E.; Weber, J. *Chem. Phys. Lett.* **1981**, *78*, 304.

(28) Kaim, W.; Ernst, S. *J. Am. Chem. Soc.* **1986**, *108*, 3578.

(29) Orgel, L. E. *J. Chem. Soc.* **1961**, 3683.

(30) Ceulemans, A.; Dendooven, M.; Vanquickenborne, L. G. *Inorg. Chem.* **1985**, *24*, 1153.

(31) Phifer, C. C.; McMillin, D. R. *Inorg. Chem.* **1986**, *25*, 1329.

(32) (a) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1985**, *119*, 61.
(b) Dodsworth, E. S.; Lever, A. B. P. *Chem. Phys. Lett.* **1986**, *124*, 152.

chemical process. The copper ion evidently adds a fifth ligand upon oxidation or releases it upon reduction.

In the TET complexes, the copper ion is in a high potential environment. $[\text{Cu}^{\text{II}}(\text{TET})](\text{ClO}_4)_2$ is reduced to the Cu(I) complex upon prolonged standing in organic solution, and the reduction is immediate on addition of a drop of H_2O_2 . This high Cu(II)/Cu(I) potential cannot be due only to the presence of π -acceptor diimine type ligands, since planar complexes of the macrocyclic bis(α -diimine) ligand TIM show very low Cu(II)/Cu(I) potentials (-0.34 V vs. NHE).³³ The geometry of the complex and the actual coordination number seem to influence the potential more than the nature of the ligand system, tetrahedral complexes showing the highest potentials. The potential of $[\text{Cu}(\text{TET})]^+$ was also found to be very sensitive to anions: if 1 equiv of tetrabutylammonium chloride is added to a TMU solution of II, the reduction wave is shifted to $+0.19$ V, indicating strong coordination of chloride ion to the Cu(II) complex. With an excess (5 equiv) of tetrabutylammonium chloride, the solution of II becomes colorless and the ligand reduction waves vanish; the cyclic voltammogram obtained is identical with that of a solution of Cu(I) without TET in TMU in the presence of an excess of chloride. The displacement of TET from Cu(I) by chloride may be reversed by addition of 10% water: the orange color of the solution is restored, and the voltammogram of II reappears. We presume this to be due to the greater solvation (and thus weaker nucleophilicity) of chloride ion in the presence of water.

Conclusions

Our objective in undertaking this work was to study the influence of the relatively rigid biphenyl group as a spacer between

two planar nitrogen-containing heterocycles. Although the flexibility of this spacer unit is limited to three torsion angles, this appears to be sufficient to allow a considerable variation in N-Cu-N angles where the two nitrogen atoms are separated by the biphenyl spacer: in the tetradentate N_2S_2 ligand 2,2'-bis-((1-phenyl-3-methyl-5-(*tert*-butylthio)pyrazol-4-ylmethylene)-amino)biphenyl⁷ the angle subtended at the copper atom by the nitrogen atoms separated by the biphenyl spacer is 94.7 (2°), whereas in the complex of Cu(II) with two 2,2'-bis(2-imidazolyl)biphenyl ligands⁸ the angles are close to 140° . The values found with TET lie between these two extremes.

The failure of TET to impose a tetrahedral geometry on Cu(II) is shown not only by the crystal structure of III but also by the strong solvent dependence shown in the electrochemical measurements. Although TET cannot impose a tetrahedral geometry, it nonetheless appears to favor this geometry, as shown by the crystal structure of III, in which a strong Cu-N bond is weakened rather than the weaker Cu-Cl bond, and by the ease with which the Cu(II) complexes are reduced to Cu(I).

Registry No. I, 16291-44-4; II, 112595-90-1; III, 112595-95-6; [Cu(TET)](ClO_4)₂, 112595-92-3; [Ni(dppe)Cl₂], 14647-23-5; [Cu(AN)₄](ClO₄), 14057-91-1; [Ni(bpy)₂]⁺, 36450-97-2; 2,2'-dilithiobiphenyl, 16291-32-0; zinc biphenyl, 112595-96-7; 6-chloro-2,2'-bipyridine, 13040-77-2.

Supplementary Material Available: Full tables of bond distances and angles and a listing of atomic displacement parameters (17 pages); a table of observed structure factors in the format of the Standard Crystallographic Data File³⁴ (50 pages). Ordering information is given on any current masthead page.

(33) Maroney, M. J.; Wicholas, M. *Inorg. Chim. Acta* 1983, 77, L237.

(34) Brown, I. D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 1983, A39, 216; 1985, A41, 399; 1988, A44, in press.

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Binuclear Complexes of the Ligand 3,6-Bis(2-pyridylthio)pyridazine Involving Homo- and Heterodiatom Binuclear Centers (Cu-Cu, Cu-Co, Cu-Zn). Crystal Structure of Bis[μ -3,6-bis(2-pyridylthio)pyridazine- N^1, μ - N^2, μ - N^3, N^4](μ -chloro)dicopper(II) Triperchlorate-Acetonitrile[†]

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Homo- and heterobinuclear complexes (Cu-Cu, Cu-Co, Cu-Zn) of the ligand PTP (3,6-bis(2-pyridylthio)pyridazine) can be generated by the unprecedented reaction of the mononuclear complex $[\text{Cu}(\text{PTP})_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ with the appropriate metal chloride salt in acetonitrile. The binuclear complexes have a unique binuclear cation $[\text{Cu}_2(\text{PTP})_2\text{Cl}]^{3+}$ ($M = \text{Cu, Co, Zn}$) involving a triple-bridging arrangement between the two square-pyramidal metal centers (two diazine bridges and a chlorine bridge). The dicopper complex exhibits fairly strong antiferromagnetic exchange ($-2J = 479$ cm^{-1}), and the copper-cobalt derivative exhibits variable-temperature magnetism indicative of an interacting $S = 1/2$, $S = 3/2$ pair with $-4J = 29 \pm 3$ cm^{-1} . The crystal and molecular structure of $[\text{Cu}_2(\text{PTP})_2\text{Cl}](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN}$ is reported. This complex crystallizes in the orthorhombic system, space group $Pm\bar{c}n$, with $a = 10.325$ (3) Å, $b = 17.917$ (5) Å, $c = 22.458$ (4) Å, and eight formula units per unit cell. A preliminary report of the structure of $[\text{CuZn}(\text{PTP})_2\text{Cl}](\text{ClO}_4)_3 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ is also described.

Introduction

Symmetrical, tetradentate (N_4) phthalazine and pyridazine ligands have been shown to form predominantly binuclear complexes, in which the diazine nitrogen pair is the binucleating focus of the ligand itself.²⁻²⁴ In a few cases, however, the ligands behave in a bidentate fashion with the formation of both mononuclear and binuclear derivatives.^{9,25-27} The ligand 3,6-bis(2-pyridyl-

thio)pyridazine (PTP, Figure 1) forms binuclear complexes $[\text{Cu}_2(\text{PTP})(\text{OH})\text{X}_3]$ ($X = \text{Cl, Br, NO}_3$), involving antiferro-

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(1) (a) Memorial University of Newfoundland. (b) National Research Council.

(2) Thompson, L. K.; Chacko, V. T.; Elvidge, J. A.; Lever, A. B. P.; Parish, R. V. *Can. J. Chem.* 1969, 47, 4141.

(3) Marongiu, G.; Lingafelter, E. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1982, B38, 620.

(4) Thompson, L. K. *Can. J. Chem.* 1983, 61, 579.

(5) Thompson, L. K.; Hartstock, F. W.; Robichaud, P.; Hanson, A. W. *Can. J. Chem.* 1984, 62, 2755.