Table VII. Thermodynamic parameters for the Comproportionation Equilibrium in DMF and DMSO (0.1 mol dm^{-3} Sodium *p*-Toluenesulfonate at 25 °C)[a]

	K_c	$-\Delta G°_c$	$-\Delta G_{stat}$	$(-\Delta G_e) + (-\Delta G_r) + (-\Delta G_s)$
DMF	3.5×10^3	4.84	0.82	4.02
DMSO	7.5×10^2	3.92	0.82	3.10

[a] All ΔG values are reported in kcal mol^{-1}.

potential (Table VI) as the dielectric constant of the solvent decreases. The difference between $E_{1/2}(1)$ and $E_{1/2}(2)$ ($\Delta E_{1/2}$ in Table VI) cannot be easily predicted, depending on the stability of the mixed-valence complex [Ni^{II}(cyclam)(ox)Ni^{III}(cyclam)]$^{3+}$ compared to that of the univalent metal complex mixture, to which some contributions can be ascribed.[36] The same contributions determine the free energy change $\Delta G°_c$ associated with the comproportionation equilibrium (3).

Comproportionation Equilibria. The stability constant associated with equilibrium 3 can be determined from the equation[37]

$$K_c = \exp((E°_2 - E°_1)F/RT) \qquad (6)$$

where $E°_1$ and $E°_2$ are the standard potentials related to the first and second oxidation steps of complex **1**. When these processes are reversible in nature, the $\Delta E_{1/2}$ value can accurately substitute the $E°_2 - E°_1$ difference and eq 6 becomes $K_c = \exp(\Delta E_{1/2}/25.69)$ at 298 K with $\Delta E_{1/2}$ given in millivolts. The free energy change $\Delta G°_c$ can be obtained from $\Delta G°_c = -RT \ln K_c$.

Four contributions have been identified in determining the magnitude of $\Delta G°_c$: (i) a statistic factor ($\Delta G_{stat} = -RT \ln 4$; 0.82 kcal mol^{-1} at 298 K) arising from the greater probability (by a factor of 4) of formation of the mixed-valence complex compared to that of the univalent mixture; (ii) an electrostatic factor (ΔG_e) due to the Coulombic interaction between the two metal centers; (iii) a contribution due to the electronic delocalization of the valence in the mixed-valence species (ΔG_r); (iv) a synergistic factor (ΔG_s) arising from the mutual stabilization between the bivalent and trivalent metal centers. In Table VII are reported the thermodynamic parameters for the comproportionation equilibrium (3) in DMF and DMSO. The values of the stability constant herein reported show that the mixed-valence species are very stable with respect to the rearrangement of the valence and that the stability decreases with the increase of the dielectric constant of the solvent. The decrease of the electrostatic interaction between the two metal centers, due to the increasing dielectric constant, lowers the value of ΔG_e; thus, K_c is greater in DMF than in DMSO.

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Registry No. **1**, 116633-72-8; [Ni$_2$(cyclam)$_2$ox]$^{3+}$, 116633-73-9; [Ni$_2$(cyclam)$_2$ox]$^{4+}$, 116633-74-0.

Supplementary Material Available: Listings of crystallographic data (Table S1), thermal parameters (Table S2), and hydrogen coordinates (Table S3) (3 pages); a listing of observed and calculated structure factors (Table S4) (12 pages). Ordering information is given on any current masthead page. A listing of experimental magnetic data is available from the authors on request.

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Structure of Tris(μ-3,5-diphenylpyrazolato-*N*,*N'*)tricopper(I). Structural Comparisons with the Silver(I) and Gold(I) Pyrazolate Trimers[†]

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Tris(μ-3,5-diphenylpyrazolato-*N*,*N'*)tricopper(I) was synthesized from CuCl and sodium 3,5-diphenylpyrazolate in the presence of 1 molar equiv of AgNO$_3$ and was characterized by single crystal X-ray analysis: triclinic, $P\bar{1}$ (No. 2), a = 13.036 (2) Å, b = 14.610 (2) Å, c = 11.674 (2) Å, α = 101.53 (1)°, β = 107.23 (1)°, γ = 100.07 (1)°, V = 2014.5 (6) Å^3, Z = 2. It consists of a nonplanar metallacycle containing a nine-membered Cu$_3$N$_6$ ring with long Cu–N bonds averaging 2.081 (7) Å. The Cu⋯Cu nonbonding distances average 3.339 (1) Å. A comparison of this complex with its isostructural silver and gold analogues showed an unexpected trend in the metal–nitrogen bond lengths with the Au–N bonds being especially short (1.98 Å).

Introduction

We have discussed recently[1] the syntheses and X-ray structures of the trimeric metallacyclic complexes [M(μ-3,5-Ph$_2$pz)]$_3$ (M = Ag^I, Au^I). Here we report the crystal structure of the isostructural [Cu^I(μ-3,5-Ph$_2$pz)]$_3$ (**1**), which completes the series of [ML]$_3$ complexes for M = d^{10}, group 11 metal and L = 3,5-Ph$_2$pz. These complexes may serve as models for the study of the reactivity of trimetallic surfaces. They also relate to studies concerned with the communication among metal ions in biological systems through conjugated bridging ligands.

The ease of oxidation of Cu^I compounds and the commonality of 3- and 4-coordination are well established.[2] Consequently, structural data for 2-coordinate Cu^I complexes are scarce.[3] The short metal–metal contacts found in such complexes have been the focus of contradicting theoretical studies.[4,20] Stable Cu^I complexes N-bound to unsaturated ligands are of particular interest, as they may relate to the reduced form of the "type 1" site of Cu-containing proteins,[5] which show an unusually high Cu^{II}/Cu^I

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[†] Abbreviations: pzH = pyrazole; pz = pyrazolate anion; 3,5-Ph$_2$pz = 3,5-diphenylpyrazolate anion; 3,5-Me$_2$pz = 3,5-dimethylpyrazolate anion; 5-Mepz = 5-methylpyrazolate anion; pz(8) identifies a μ-3,5-diphenylpyrazolate ring by using the crystallographic numbering scheme of the carbon at the 4-position of that ring.

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Table I. Crystallographic Data for $[Cu(\mu\text{-}3,5\text{-}Ph_2pz)]_3\cdot{}^1/_2C_6H_{14}$

formula	$C_{48}H_{40}Cu_3N_6$
fw	891.53
space group	$P\bar{1}$ (No. 2)
a, Å	13.036 (2)
b, Å	14.610 (2)
c, Å	11.674 (2)
α, deg	101.53 (1)
β, deg	107.23 (1)
γ, deg	100.07 (1)
V, Å^3	2014.5 (6)
Z	2
d_{calc}, g/cm^{-3}	1.47
μ(Mo Kα), cm^{-1}	16.15
radiation λ, Å (monochromated in Mo Kα)	0.71069
temp, °C	22
trans factors: max, min	0.924, 0.781
R^a	0.0636
$R_w{}^b$	0.0708

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$.

redox potential. The copper atoms at such sites were found by X-ray analyses[6] to be in a distorted-tetrahedral environment, coordinated to two histidine nitrogen atoms and two cysteine and methionine sulfur atoms. On the other hand, in some binuclear "type 3" sites,[7] the Cu^I atoms were found by EXAFS studies[8] to be coordinated either by only two nitrogen atoms at distances of 1.95–2.00 Å or by three nitrogen atoms with the third one at a significantly longer distance from Cu, 2.26 Å.

The syntheses of copper(I) pyrazolates were first reported[9] in the last century; however, their structural characterization has been elusive. $[Cu(3,5\text{-}Me_2pz)]_n$ was found[10] to be polymeric, while Cu(5-Mepz) was reported[11] as "at least trimeric" on the basis of mass spectroscopic data. A $Cu^{II}{}_3N_6$ metallacycle was found in the crystal structure[12] of $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3(pzH)_2(NO_3)_2]\cdot H_2O$ obtained by the air oxidation of $[Cu(pzH)_2(NO_3)]$.

Experimental Section

Synthesis. All reactions were carried out under an argon atmosphere by using Schlenk techniques.[13] 3,5-Diphenylpyrazole, purchased from Lancaster Synthesis Ltd., was deprotonated with NaH in tetrahydrofuran, and the product was precipitated by addition of hexane. The reaction of CuCl (20 mg, 0.20 mmol) with $AgNO_3$ (34 mg, 0.20 mmol) and $Na[3,5\text{-}Ph_2pz]$ (73 mg, 0.30 mmol) in 10 mL of CH_2Cl for 16 h gave 40 mg of a colorless product consisting of $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3$[1] (>80%), lesser amounts of $[Ag_xCu_y(\mu\text{-}3,5\text{-}Ph_2pz)_3]$, $x + y = 3$ (by mass spectroscopy and C, H, N analysis), and $[Cu(\mu\text{-}3,5\text{-}Ph_2pz)]_3$, (**1**) as a minor product. Recrystallization from CH_2Cl_2/Et_2O at −5 °C gave colorless, air-stable crystals of **1**. These were visually separated from the crystals of the silver-containing materials, which upon exposure to air became opaque due to rapid solvent loss.[1]

Crystallography. The X-ray analysis of **1** was carried out with a Nicolet R3m/E automated diffractomer and SHELXTL software implemented on an Eclipse S140 minicomputer, as has been described elsewhere.[14] A single crystal of **1** appropriate for X-ray study was mounted atop a glass fiber for data collection. Initial cell parameters were determined by using orientation reflections obtained from photographic data and were confirmed by axial photographs and a Delaunay reduction. Accurate unit cell dimensions were calculated from the setting angles of 25 reflections with 30° < 2θ < 35°. Intensity data were collected for 7091 unique reflections, $+h$, $\pm k$, $\pm l$ with 0° < 2θ < 50°, by using the ω-scanning technique in bisecting geometry. No symmetry-equivalent reflections were measured. The intensity data were corrected for Lorentz and polarization effects; no standard decay was observed during data collection. An empirical absorption correction based on azimuthal scans of medium-intensity reflections was applied. Initial positional parameters for the three copper atoms were obtained from a sharpened Patterson map. The remaining non-hydrogen atoms were located in difference

Table II. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for $[Cu(\mu\text{-}3,5\text{-}Ph_2pz)]_3$

	x	y	z	U^a
Cu(1)	8177 (1)	2056 (1)	3635 (1)	34 (1)*
Cu(2)	9886 (1)	6447 (1)	3883 (1)	38 (1)*
Cu(3)	806 (1)	1758 (1)	4503 (1)	39 (1)*
N(1)	−2096 (5)	3407 (4)	4227 (6)	68 (3)*
N(2)	−1266 (5)	3998 (5)	5336 (6)	69 (3)*
N(3)	1664 (5)	3313 (5)	6832 (7)	71 (3)*
N(4)	2049 (5)	2852 (5)	5937 (6)	70 (3)*
N(5)	−478 (5)	563 (4)	3347 (6)	65 (3)*
N(6)	−1560 (5)	682 (4)	3069 (6)	68 (3)*
C(1)	−2827 (6)	3895 (5)	3788 (7)	62 (3)*
C(2)	−2499 (7)	4830 (5)	4590 (8)	71 (4)*
C(3)	−1506 (7)	4881 (5)	5551 (8)	65 (3)*
C(4)	12545 (6)	3863 (5)	7832 (7)	63 (3)*
C(5)	3529 (6)	3764 (5)	7586 (7)	65 (3)*
C(6)	3189 (6)	3118 (5)	6369 (7)	60 (3)*
C(7)	−564 (7)	−369 (5)	3048 (7)	65 (3)*
C(8)	−1674 (6)	−861 (5)	2585 (7)	64 (3)*
C(9)	−2248 (6)	−178 (5)	2639 (7)	60 (3)*
C(11)	5252 (5)	3879 (4)	2617 (5)	89 (5)*
C(12)	4293	3521	1567	118 (6)*
C(13)	4254	2785	576	119 (6)*
C(14)	5174	2407	635	110 (5)*
C(15)	6133	2765	1685	81 (4)*
C(16)	6172	3502	2676	71 (4)*
C(31)	8640 (5)	6411 (5)	6972 (6)	121 (6)*
C(32)	9238	7201	7993	149 (9)*
C(33)	10351	7285	8641	139 (7)*
C(34)	10867	6577	8269	102 (5)*
C(35)	10270	5787	7248	90 (5)*
C(36)	9156	5704	6599	72 (4)*
C(41)	13263 (4)	5280 (4)	9640 (5)	78 (4)*
C(42)	13180	5837	10713	98 (5)*
C(43)	12272	5558	11075	107 (6)*
C(44)	11446	4721	10365	102 (6)*
C(45)	11528	4164	9292	80 (4)*
C(46)	12437	4444	8929	65 (3)*
C(61)	14976 (4)	3318 (3)	6052 (5)	80 (4)*
C(62)	15675	3000	5445	87 (5)*
C(63)	15272	2161	4464	91 (5)*
C(64)	14170	1641	4090	115 (6)*
C(65)	13471	1959	4697	84 (4)*
C(66)	13874	2798	5678	66 (3)*
C(71)	286 (4)	−1630 (4)	2237 (4)	79 (4)*
C(72)	1165	−2067	2312	91 (5)*
C(73)	2167	−1673	3299	89 (5)*
C(74)	2290	−842	4211	87 (4)*
C(75)	1411	−406	4136	76 (4)*
C(76)	409	−800	3149	62 (3)*
C(91)	−4025 (4)	−1050 (4)	2684 (5)	80 (4)*
C(92)	−5159	−1187	2471	100 (6)*
C(93)	−5734	−582	1908	92 (5)*
C(94)	−5175	159	1559	81 (4)*
C(95)	−4041	296	1772	73 (4)*
C(96)	−3466	−309	2335	61 (3)*
C(1*)	274	548	334	200
C(2*)	1237 (12)	77 (12)	223 (18)	200
C(3*)	2255 (14)	776 (13)	701 (17)	200

[a] Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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Table III. Distances (Å) and Angles (deg) for $[Cu(\mu\text{-}3,5\text{-}Ph_2pz)]_3$

	Distances		
Cu(1)···Cu(2)	3.280 (1)	N(1)–C(1)	1.332 (1)
Cu(1)···Cu(3)	3.406 (1)	N(2)–C(3)	1.372 (1)
Cu(2)···Cu(3)	3.332 (1)	N(3)–C(4)	1.355 (8)
Cu(1)–N(1)	2.085 (7)	N(4)–C(6)	1.374 (1)
Cu(1)–N(6)	2.105 (7)	N(5)–C(7)	1.313 (1)
Cu(2)–N(2)	2.041 (7)	N(6)–C(9)	1.312 (8)
Cu(2)–N(3)	2.066 (7)	C(1)–C(2)	1.41 (1)
Cu(3)–N(4)	2.098 (5)	C(2)–C(3)	1.42 (1)
Cu(3)–N(5)	2.090 (5)	C(4)–C(5)	1.42 (1)
N(1)–N(2)	1.410 (7)	C(5)–C(6)	1.43 (1)
N(3)–N(4)	1.394 (11)	C(7)–C(8)	1.39 (1)
N(5)–N(6)	1.401 (10)	C(8)–C(9)	1.35 (1)
	Angles		
N(1)–Cu(1)–N(6)	178.6 (3)	Cu(2)–N(3)–N(4)	114.4 (5)
N(2)–Cu(2)–N(3)	169.6 (3)	Cu(3)–N(4)–N(3)	113.1 (5)
N(4)–Cu(3)–N(5)	169.2 (3)	Cu(3)–N(5)–N(6)	116.9 (4)
Cu(1)–N(1)–N(2)	113.7 (5)	Cu(1)–N(6)–N(5)	120.0 (4)
Cu(2)–N(2)–N(1)	120.2 (5)		

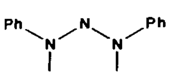
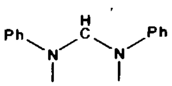
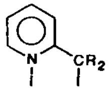
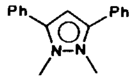
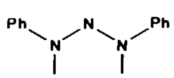
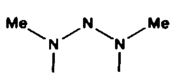
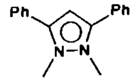
Fourier maps. An interstitial molecule of hexane was found to occupy the site of a center of symmetry and was treated with its positional and isotropic thermal parameters fixed. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.960 Å), and phenyl groups were treated as idealized rigid hexagons (C–C = 1.395 Å, C–C–C = 120°) to minimize parametrization. The weighting scheme employed a *g* value that was first refined and then fixed at 0.003 during the last cycle of refinement. Structure refinement using all 7091 unique reflections gave an *R* value of 0.0765. Refinement of 421 parameters using 5553 reflections with $F_o^2 > 3\sigma(F_o^2)$ converged to a conventional *R* value of 0.0636 with a goodness-of-fit indicator of 1.684. The highest peak of residual electron density, 1.20 e Å^{-3}, appears at a distance of 0.19 Å from Cu(1). At that point, the unaccounted for electron density was suspected to result from the presence of some silver impurity in the crystal. Therefore, a silver atom was included in the structure model. Its positional parameters were tied to those of Cu(1), and the occupancy factors of the two atoms, Cu(1) and Ag, were tied together so that their sum equaled 1.0. Refinement of this model gave negative-site occupancy for the Ag atom. Parameters pertaining to data collection and structure refinement are listed in Table I. Atomic coordinates and equivalent isotropic thermal parameters for **1** are given in Table II. Tables of observed and calculated structure factors with their esd's, listings of anisotropic thermal parameters and hydrogen coordinates and isotropic thermal parameters, and complete lists of crystallographic data, bond lengths, and bond angles for **1** have been deposited as supplementary material.

Results and Discussion

The reactions of CuCl with $Na[3,5\text{-}Ph_2pz]$ in a variety of solvents of ambient temperature gave either oxidized Cu^{II} materials[15] (air-oxidation or disproportionation reactions) or no detectable amount of product. A small amount of the desired product **1** was successfully synthesized by initiating the reaction with the addition of $AgNO_3$ to precipitate the Cl^- ions.

The structure of **1** consists of a nine-membered $(Cu^I\text{–}N\text{–}N)_3$ metallacyclic ring (Figure 1) similar to the ones of the isostructural Ag^I and Au^I compounds.[1] Complex **1** shows significant deviations from planarity (Figure 2), resembling in this regard the Ag trimer[1] and contrasting the rigorously planar Au trimer.[1] The nitrogen atoms deviate as much as 0.744 Å (N(6)) from the plane of the three copper atoms. One pyrazolate ring, pz(8), is below this plane, a second one, pz(2), is above, and the third one, pz(5), is rotated and bisected by the Cu_3 plane to accommodate the twist of the Cu_3N_6 ring. The coordination around Cu(1) is almost linear, 178.6 (3)°, while the N–Cu–N angles of Cu(2) and Cu(3) are 169.6 (3) and 169.2 (3)°, respectively. The N–N–Cu angles for the sp^2-hybridized nitrogen atoms show only small deviations from 120°, the largest one observed on N(4), 113.1 (5)°. The Cu–N bond lengths are unusually long (vide infra) ranging from 2.041 (7) to 2.105 (7) Å with an average length of 2.081 (7) Å. As no significant deviations from ideal geometry are observed at the copper and nitrogen atoms, the twisting of the metallacycle is observed primarily in the Cu–N–N–Cu dihedral angles, 5.6, 39.7,

Table IV. M–N Bond Lengths (Å) for $[ML]_n$ Complexes

	M–N measd							
	L in $[ML]_2$			L in $[ML]_3$	L in $[ML]_4$		L in $[ML]_6$	
M^I								M–M estd[j]
Cu	1.90 (2)[a]	1.886 (7)[c]	1.910 (3)[d]	2.041 (7)–2.105 (7)[e]				2.04
	1.94 (2)	1.859 (7)						
	1.92 (2) av	1.873 (7) av		2.081 (7) av		1.87 (3)[h] av		
Ag	2.155 (3)[b]	2.116 (5)[c]	2.160 (5)[d]	2.08 (1)–2.09 (1)[f]				2.19
	2.144 (4)	2.094 (5)						
	2.150 (4) av	2.105 (5) av		2.085 (10) av				
Au			2.081 (11)[d]	1.978 (9)[f]	2.018 (5)–2.066 (5)[a]		2.00 (3)–2.16 (3)[i]	2.06
							2.06 (3) av	

[a] Reference 18. [b] Reference 19. [c] Reference 20. [d] Reference 16. [e] This work. [f] Reference 1. [g] Reference 21. [h] Reference 22. [i] References 1 and 23. [j] Reference 17; M–N = $r_M + r_N - 0.07|x_M - x_M|^2$; r_M, r_N, x_M, and x_N are the covalent radii and Pauling electronegativities for M and N, respectively.

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(15) Raptis, R. G.; Fackler, J. P., Jr., unpublished results.

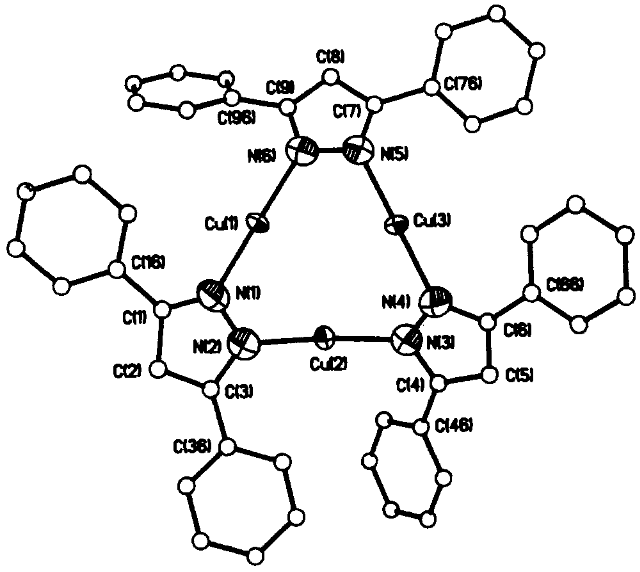

Figure 1. ORTEP drawing of $[Cu(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ with the crystallographic numbering scheme. The carbon atoms have been given arbitrary radii. Thermal ellipsoids are drawn at the 50% probability level.

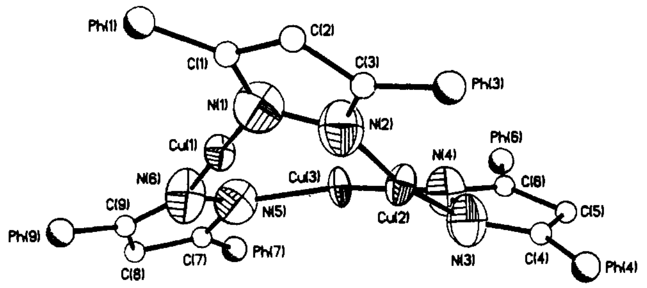

Figure 2. ORTEP drawing of $[Cu(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ depicting the twist of the nine-membered metallacycle. Phenyl groups are represented by their ipso carbon atoms for clarity. Carbon atoms have been arbitrary radii. Thermal ellipsoids are drawn at the 50% probability level.

and 7.0° for pz(2), pz(5), and pz(8), respectively (Figure 2). The twisting of the Cu_3N_6 ring is attributed to packing forces and the flexibility of Cu^I–N bonds. The Cu···Cu nonbonding distances range between 3.280 (1) and 3.406 (1) Å with an average of 3.339 (1) Å. Some important angles and distances for **1** are summarized in Table III.

A comparison of the structural features of the grossly isostructural complexes $[M(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ ($M = Cu^I, Ag^I, Au^I$) is made here, as there is only one other example[16] of a complete isostructural series for the group 11 metals. The intermetallic distances for the Au and Ag trimers,[1] 3.368 (1) Å for Au and 3.305 (2)–3.496 (2) Å for Ag, are comparable to the sums of the van der Waals atomic radii,[17] so that the three Au atoms (radius 1.66 Å) make a snug fit into the cavity defined by the six nitrogen atoms, while in the Ag analogue (radius 1.72 Å) the metal atoms are somewhat crowded. In contrast, the metal atoms of **1** are separated by an average distance of 3.339 (1) Å, which is approximately 17% longer than the sum of their van der Waals radii, 2.86 Å, thus leaving a "hole" of radius ~0.50 Å at the center of the trinuclear unit. This metal–metal distance compares well with the average Cu^{II}–Cu^{II} distance, 3.351 (7) Å, of a trinuclear $(Cu^{II}pz)_3$ unit that is capped by a μ_3-OH group.[12] The Cu–Cu distances measured in **1** approximate the ones determined by EXAFS, 3.43 (5)–3.48 (5) Å[8a–c] and 3.39 (5) Å,[8d] for the binuclear active sites of hemocyanins, containing 2- or 3-coordinate, imidazole-bound Cu^I atoms.[8] The Cu–N bond lengths of **1**, 2.041 (7)–2.105 (7) Å, are longer than those of the hemocyanin copper site. They compare well, however, with the Cu–N bonds[6b] of the 4-coordinate type 1 site for both Cu^I and Cu^{II} oxidation states, 2.07, 2.82 and 2.10, 2.04 Å, respectively. A special feature of this isostructural series is that the M–N bond length for M = Au is ~0.10 Å shorter than those for both M = Ag and M = Cu. Table IV is a listing of M^I–N bond lengths from some complexes of the type $[ML]_n$, where M is a group 11 metal and L is a nitrogen-donor ligand. The last column of Table IV gives the M^I–N single-bond lengths for Cu, Ag, and Au as they are estimated[17] from their covalent radii with an empirical correction for the electronegativity difference between M and nitrogen. When the bond lengths measured in the series $[M(\mu\text{-}3,5\text{-}Ph_2pz)]_3$ are compared with the calculated values, there is good agreement for Cu, while the measured bonds for Ag and Au are significantly shorter than the predicted values. The opposite is observed[16] in the series $[M(\mu\text{-}2\text{-}C(SiMe_3)_2C_5H_4N)]_2$; namely, there is agreement between measured and estimated bond lengths for Ag and Au, but not for Cu. The bond lengths observed by Papasergio et al.[16] are consistent with the results for all other Cu and Au complexes listed in Table IV, while $[Ag(PhNCHNPh)]_2$ is an exception having bonds ~0.1 Å shorter[20] than predicted.

In the absence of steric interactions, the long Cu–N bonds of **1** suggest that there is no π-back-bonding contribution to the bonding scheme of this complex, consistent[24] with the observation of the absence of color in this material. By contrast, it appears that there is significant back-donation from the gold $5d^{10}$ orbitals into the π^* system of the pyrazolate ring. In the similar complex $[Au(\mu\text{-}3,5\text{-}(CF_3)_2pz)]_3$, containing the strongly electron-withdrawing CF_3 group, the Au–N bonds are even shorter, 1.93 (1) Å.[25] It is interesting that when the planarity of the metallacyclic ring is disturbed, as is the case[23] for the hexameric $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_6$ containing an 18-membered $(Au\text{–}N\text{–}N)_6$ ring in the shape of a two-bladed propeller, a pronounced elongation of the Au–N bonds results. The average Au–N bond length of this complex, 2.06 (3) Å, approaches the M–N bond lengths of the homologous Cu and Ag trimers (see Table IV). Nothing obvious precludes the synthesis of hexameric Cu and Ag diphenylpyrazolates.

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Registry No. **1**, 116785-35-4; $[Ag(\mu\text{-}3,5\text{-}Ph_2pz)]_3$, 111495-79-5.

Supplementary Material Available: Tables SI–SV, listing crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for **1** (4 pages); Table SVI, listing observed and calculated structure factors for **1** (42 pages). Ordering information is given on any current masthead page.

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