Table VII

Bond type	$\bar{\nu}$, cm^{-1}	Bond length, Å	
		Av	Range
Linear terminal	1850–1650[a]	1.19	1.12–1.23[b]
Doubly bridging			
$Ru_3(CO)_{10}(NO)_2$	1503–1475[c]	1.22	1.20–1.24
$(\eta^5\text{-}C_5H_5)_2Mn_2(NO_2)(NO)_3$		1.205[d]	
$(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_4$	1530–1480[e]	1.212	1.207–1.218
Triply bridging			
$(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_4$	1320[e]	1.247	

[a] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 7, 277 (1966). [b] See ref 19, 30–37. [c] See ref 40. [d] See ref 19. [e] This work.

survey[19,30–37] of the literature shows a wide range of NO distances. However, the average, 1.19 Å, appears to be a reasonable value.[38] At least four crystal structures[19,39,40] are known to contain doubly bridging nitrosyls. The average value found here of 1.212 (6) Å for the doubly bridging NO bond falls in the range of those previously determined. The triply bridging nitrosyl (1.247 (5) Å) appears to be the only one reported and it has both the lowest infrared stretching frequency (1320 cm^{-1}) and the longest NO bond length so far observed.

Fackler and Coucouvanis[41] have attempted to show a linear relationship between bond orders and the square of the associated stretching frequency for CO, CN, and NO, with considerable success in the first two cases. Following their methods, the doubly bridging bond order for NO is calculated to be 1.72 and that for triply bridging NO is 1.56. However, the predicted stretching frequencies (1675 and 1575 cm^{-1}) are much too high[42] and the method fails for NO.

Acknowledgments. The author thanks Professor F. A. Cotton and Dr. R. A. Schunn for bringing the problem to his attention, Professor L. F. Dahl and Dr. B. K. Teo for suggesting a solution, and Dr. L. R. Florian, who measured the data.

Registry No. $(\eta^5\text{-}C_5H_5)_3Mn_3(\mu_3\text{-}NO)(\mu_2\text{-}NO)_3$, 12312-71-9.

Supplementary Material Available. A listing of the structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1037.

(31) M. A. Busch, G. Sim, G. A. Knox, and C. G. Robertson, *Chem. Commun.*, 74 (1969).

(32) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 10, 1479 (1971).

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(34) J. H. Enemark, *Inorg. Chem.*, 10, 1952 (1971).

(35) J. H. Enemark, M. S. Quimby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, 9, 2397 (1970).

(36) R. Eisenberg, A. P. Gaughan, Jr., C. G. Pierpoint, J. Reed, and A. J. Schultz, *J. Amer. Chem. Soc.*, 94, 6240 (1972).

(37) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 7, 2339 (1968).

(38) A referee has kindly pointed out a recent review (B. A. Frenz and J. A. Ibers in "MTP International Review of Science, Physical Chemistry Series One," Vol. 11, J. M. Robertson, Ed., Butterworths, London, 1972, Chapter 2) in which the average NO distance is given as 1.17 Å.

(39) L. Y. Y. Chan and F. W. B. Einstein, *Acta Crystallogr., Sect. B*, 26, 1899 (1970). This structure suffers from at least two kinds of disorder and shows an extremely short doubly bridging NO distance of 1.121 (22) Å. This somewhat suspicious value has been omitted from Table VII.

(40) J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 11, 382 (1972).

(41) J. P. Fackler and D. Coucouvanis, *Inorg. Chem.*, 7, 181 (1968).

(42) Indeed, the two points generated here fall on the same line as two other cases [$Fe(CO)_2(NO)_2$ and $Co(NO)(CO)_3$] which were considered anomalous.

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Structure of the Dimetallic Complex *catena*-μ-Chloro-dichloro-μ-[*N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinedicarboxamidato-*N,N*^{N}*,N*^{1}*:N',N*$^{N'}$*,N*^{4}]-dicopper

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The crystal structure of the complex Cu_2LCl_3, *catena*-μ-chloro-dichloro-μ-[*N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinedicarboxamidato-*N,N*^{N}*,N*^{1}*:N',N*$^{N'}$*,N*^{4}]-dicopper, was determined by a complete three-dimensional X-ray analysis. The structure of the compound is that of a bimetallic (two cupric ions) complex with both copper ions similarly bound by one of the pyrazine nitrogens, a deprotonated amide nitrogen, a pyridine nitrogen, and two chloride ions. The pseudo-trigonal-bipyramidal geometry is accomplished in the crystal by a chloride ion bridging between the complexes forming an infinite-chain structure in the solid. The crystal is in the space group $P2_1/c$ with four molecules per cell. The cell constants for the monoclinic system are a = 7.95 (1) Å, b = 27.00 (3) Å, c = 10.25 (1) Å, and β = 92.1 (1)°, and the observed density of 1.86 g/cm^3 agrees well with the calculated density of 1.85 g/cm^3. The structure was refined by a least-squares technique with 1941 structure factor amplitudes collected on a diffractometer to an R factor of 4.2%. The temperature-dependent magnetic susceptibility was measured for the complex and is suggestive of a weak antiferromagnetic interaction in the system.

We have previously synthesized[1] the ligand *N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinedicarboxamide, Figure 1 (hereafter abbreviated in the paper as L), and prepared some transition metal complexes of it. One of the complexes of interest is with cupric ion and has the formulation of Cu_2LCl_3. The stoichiometry with the three chlorides was interesting because it implied that one of the amide protons was lost

(1) E. B. Fleischer and M. B. Lawson, *Inorg. Chem.*, 11, 2772 (1972).

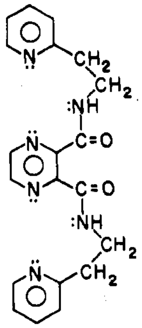

Figure 1. The ligand *N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinecarboxamide.

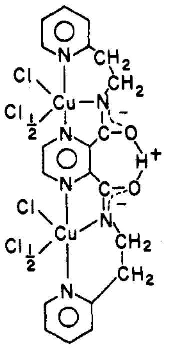

Figure 2. Formulation of the copper complex Cu_2LCl_3.

and it was not easy straightforwardly to deduce the structure from the spectroscopic properties. We have an interest in preparing bimetallic complexes with ligands that would allow for possible interactions between the metal centers *via* the ligand π system.[2,3] The structure of the Cu_2LCl_3 is described in this paper and it is clear from the structural study that the complex has the rather interesting formulation given in Figure 2. Thus in the complex both copper ions are bonded to the pyrazine moiety and both amide protons are lost; one of the protons moves between the two carbonyl oxygens.

Experimental Section

Dark green needle-shaped crystals of $Cu_2Cl_3(C_{20}H_{19}N_6)$ were obtained by the method previously described.[1] Precession photographs of the *hk*0, *h*0*l*, *hk*1, and *h*1*l* zones showed systematic absences of 0*k*0 for *k* odd and *h*0*l* for *l* odd. The unique monoclinic space group $P2_1/c$ was indicated.

Crystals more suitable for data collection were obtained by dissolving $CuCl_2 \cdot 2H_2O$ in hot water along with a tenfold excess of KCl. To this solution was added a stoichiometric amount L also dissolved in hot water. The ligand is that reported previously in the literature.[1] When the dark blue solution of the complex was allowed to cool, dark green crystals were formed. The solution was filtered and the crystals were washed with methanol. A tablet-shaped crystal of dimensions 0.1 mm × 0.2 mm × 0.3 mm was mounted on a glass fiber with the long dimension of the crystal parallel to the fiber axis. Precession photographs of the *h*0*l*, *h*0*l*, and *hk*1 zones showed the same absences and lattice constants as those of the above-described needle-shaped crystals. The two sets of crystals although grown differently were considered to be identical in composition.

The crystal was then mounted on a Picker four-circle X-ray diffractometer and using Mo Kα radiation 13 reflections were individually centered. Least-squares refinement of the setting angles, χ, ϕ, and 2θ, of these reflections gave lattice constants $a = 7.95$ (1) Å, $b = 27.00$ (3) Å, $c = 10.25$ (1) Å, and $\beta = 92.1$ (1)°. The calculated density 1.85 g/cm³ based on four molecules per unit cell agreed with the measured density 1.86 (2) g/cm³ (neutral buoyancy method).

Table I. Atomic Positional Parameters (Fractional Coordinates)

Atom	*x*	*y*	*z*
Cu_1	0.3315 (1)	0.0603 (4)	0.2301 (1)
Cu_2	1.0563 (1)	0.1485 (1)	−0.0095 (1)
Cl_1	0.1985 (3)	0.0614 (1)	0.0198 (2)
Cl_2	0.9667 (3)	0.1482 (1)	−0.2194 (2)
Cl_3	0.4212 (3)	−0.0229 (1)	0.2685 (2)
N_1	0.1105 (9)	0.0516 (2)	0.3154 (6)
N_2	0.4281 (9)	0.1041 (3)	0.3654 (6)
N_3	0.5522 (8)	0.0820 (2)	0.1491 (6)
N_4	0.8446 (8)	0.1167 (2)	0.0549 (6)
N_5	1.0398 (9)	0.1815 (2)	0.1592 (7)
N_6	1.2787 (9)	0.1782 (3)	−0.0489 (7)
O_1	0.6433 (8)	0.1551 (2)	0.4317 (6)
O_2	0.8827 (7)	0.1915 (2)	0.3383 (6)
C_1	0.0077 (11)	0.0173 (3)	0.2612 (8)
C_2	−0.1464 (11)	0.0065 (3)	0.3099 (9)
C_3	−0.1964 (12)	0.0299 (3)	0.4222 (9)
C_4	−0.0908 (12)	0.0647 (3)	0.4780 (8)
C_5	0.0608 (11)	0.0747 (3)	0.4228 (8)
C_6	0.1694 (13)	0.1169 (4)	0.4800 (10)
C_7	0.3519 (13)	0.1076 (4)	0.4938 (9)
C_8	0.5665 (11)	0.1265 (3)	0.3472 (8)
C_9	0.6438 (10)	0.1154 (3)	0.2194 (8)
C_{10}	0.6079 (10)	0.0651 (3)	0.0390 (8)
C_{11}	0.7573 (10)	0.0822 (3)	−0.0098 (8)
C_{12}	0.7932 (10)	0.1333 (3)	0.1709 (8)
C_{13}	0.9114 (10)	0.1718 (3)	0.2286 (8)
C_{14}	1.1547 (12)	0.2207 (4)	0.2062 (9)
C_{15}	1.2211 (13)	0.2494 (3)	0.0930 (9)
C_{16}	1.3343 (11)	0.2207 (3)	0.0073 (8)
C_{17}	1.4954 (13)	0.2376 (4)	−0.0170 (11)
C_{18}	1.5959 (12)	0.2120 (4)	−0.1011 (11)
C_{19}	1.5311 (13)	0.1701 (4)	−0.1618 (10)
C_{20}	1.3743 (12)	0.1545 (4)	−0.1320 (9)
H_1	0.0490	−0.0033	0.1762
H_2	−0.2304	−0.0205	0.2599
H_3	−0.3156	0.0213	0.4650
H_4	−0.1281	0.0847	0.5654
H_5	0.1221	0.1283	0.5739
H_6	0.1543	0.1494	0.4141
H_7	0.3710	0.0723	0.5480
H_8	0.4153	0.1362	0.5539
H_9	0.5326	0.0374	−0.0169
H_{10}	0.8042	0.0673	−0.1004
H_{11}	1.0885	0.2455	0.2704
H_{12}	1.2598	0.2043	0.2625
H_{13}	1.1151	0.2629	0.0325
H_{14}	1.2916	0.2816	0.1297
H_{15}	1.5429	0.2719	0.0327
H_{16}	1.7243	0.2247	−0.1184
H_{17}	1.6073	0.1499	−0.2307
H_{18}	1.3223	0.1215	−0.1817
H_{19}	0.7713	0.1787	0.3835

Diffraction data were collected by use of procedures described previously.[4,5] In this case the diffracted beam was filtered through a 3.0-mm Nb foil. A takeoff angle of 2.0° was used. The counter aperture was 5 mm × 5 mm and positioned 29 cm from the crystal. A 2θ scan range of ±0.5° from the calculated 2θ value was used for all reflections. The scan rate was 1°/min and stationary-background counts of 20 sec were taken at each end of the scan range.

A total of 2839 reflections were measured for $2\theta \leqslant 43°$, of which 1941 were above background by more than three standard deviations and were thus treated as observed. The *p* factor used in calculating $\sigma(I)$ was assigned a value of 0.05 where $\sigma(I) = [C + 0.25(t_c/t_b)^2 \cdot (B_1 + B_2) + (pI)^2]^{1/2}$.

Four standards were measured after every 100 reflections. The decrease in intensity of these standards over the period of data collection was less than 1% so no intensity correction of the data based on the intensities of these standards was applied. The data were corrected for background and Lorentz polarization. The linear absorption coefficient for this compound is 18.7 cm⁻¹. The minimum and maximum values of μR are 0.09 and 0.20, respectively. Since the maximum relative error in F_o would be less than 3%, no absorption correction was made.

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(2) E. B. Fleischer and M. B. Lawson, *J. Coord. Chem.*, **2**, 79 (1972).

(3) E. B. Fleischer and D. Lavallee, *J. Amer. Chem. Soc.*, **94**, 2583 (1972).

(4) P. W. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(5) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

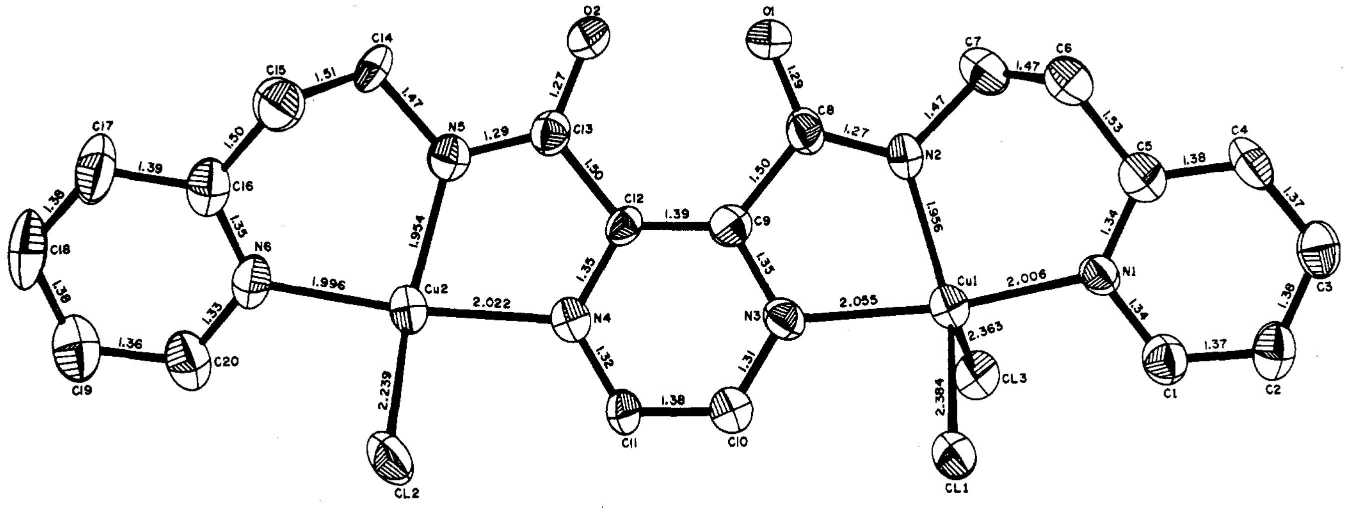

Figure 3. Numbering scheme and bond distances for the complex Cu_2LCl_3.

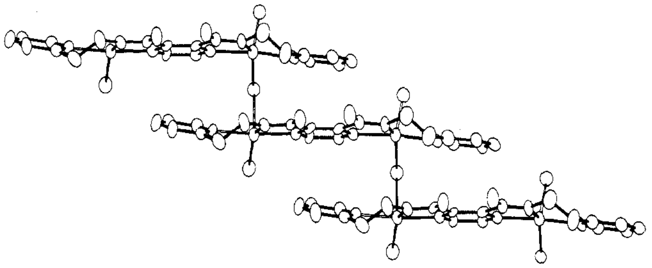

Figure 4. Structure of Cu_2LCl_3 showing the relationship of the chloride bridges to the polymeric structure of the complex.

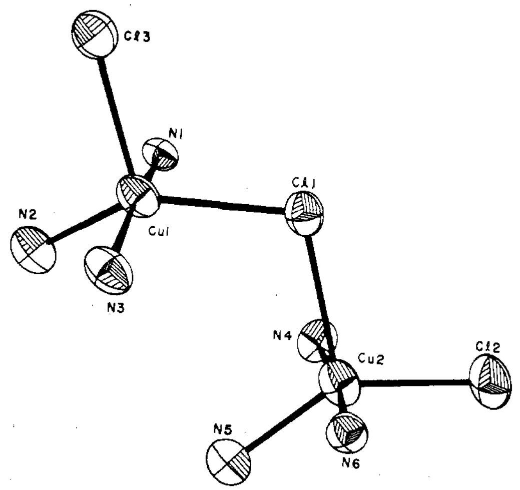

Figure 5. Coordination sphere of the copper ions in the Cu_2LCl_3 complex.

Solution and Refinement of the Structure. The structure was solved using heavy-atom methods. The positions of the two copper atoms were determined from a Patterson function and the positions of the rest of the nonhydrogen atoms were located from a difference map. Full-matrix least-squares refinement, using unit weights, gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.058$. The two copper atoms and the three chlorine atoms were refined using anisotropic temperature parameters while isotropic temperature parameters were used for the rest of the nonhydrogen atoms. At this point the positions of the 18 hydrogen atoms bonded to carbon were calculated (C–H = 1.05 Å) and added to the refinements. However, the positional and isotropic thermal parameters of the hydrogen atoms were not varied. A difference map was calculated and the final hydrogen was found. Thus, the position of this hydrogen was determined to be between the two carbonyl oxygens rather than within bonding distance to either amine nitrogen.

With addition of the parameters of the final hydrogen, the refinement was continued with all nonhydrogen atoms varied anisotropically. None of the hydrogen atom parameters were varied. The last cycle of refinement converged to $R = 4.2\%$ with the largest parameter shift equal to 0.13σ.

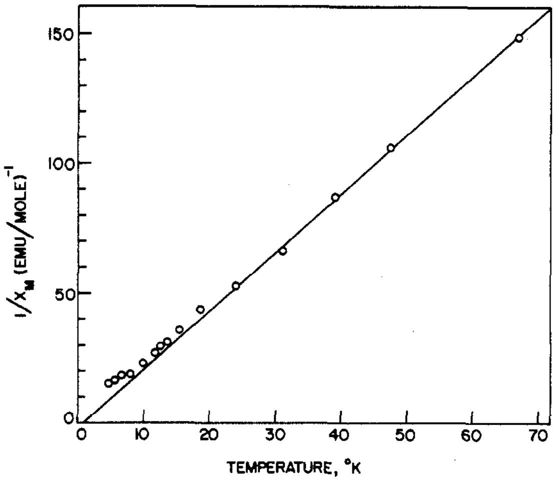

Figure 6. Temperature-dependent magnetic susceptibility of the Cu_2LCl_3 complex.

Examination of R factors computed for groups of reflections ordered on $(\sin\theta)/\lambda$ and computed for groups ordered on $|F_o|$ showed no unusual trends. Consequently unit weights were used and considered appropriate for the least-squares refinement.

Atomic scattering factors of Cu were taken from Cromer and Waber,[6] those for H from Stewart, Davidson, and Simpson,[7] and all others from the appropriate tabulation.[8] The values for the allowance of anomalous scattering for Cu and Cl were taken from the tabulation of Cromer.[9] A listing of the observed diffraction data is available.[10] Figure 3 gives the numbering system employed in the crystallographic study and also shows some of the bond distances in the complex.

(6) D. J. Cromer and J. T. Weber, *Acta Crystallogr.*, 18, 104 (1965).

(7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(8) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

(9) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(10) This refinement made use of J. A. Iber's diffractometer setting program PICK. Other computer programs used in this work include local versions (for use on a PDP-10 computer) of PICKOUT (R. J. Doedens, J. A. Ibers) for data processing, GONO (W. C. Hamilton) for absorption correction, FORDAP (A. Zalkin) for Fourier summation, UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement, ORFFE (Busing, Martin, and Levy) for function and error calculations, PLANET (D. L. Smith) for least-squares plane calculations, DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of the figures, RSCAN (R. J. Doedens) for evaluation of weighting scheme, and various local programs.

Table II. Thermal Parameters

Atom	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu_1	0.0097 (2)	0.00105 (2)	0.00627 (11)	−0.00051 (5)	0.00225 (11)	−0.00039 (3)
Cu_2	0.0106 (2)	0.00124 (2)	0.00659 (12)	−0.00095 (5)	0.00219 (12)	−0.00026 (4)
Cl_1	0.0110 (4)	0.00119 (4)	0.0059 (2)	−0.00026 (10)	0.0011 (2)	−0.00003 (7)
Cl_2	0.0140 (5)	0.00209 (5)	0.0058 (2)	−0.00067 (13)	0.0021 (3)	−0.00013 (8)
Cl_3	0.0117 (4)	0.00102 (3)	0.0071 (2)	−0.00019 (10)	0.0004 (2)	−0.00013 (7)
N_1	0.014 (1)	0.0007 (1)	0.0054 (7)	−0.0007 (3)	0.0036 (8)	−0.0002 (2)
N_2	0.011 (1)	0.0012 (1)	0.0071 (8)	−0.0011 (4)	0.0034 (9)	−0.0004 (3)
N_3	0.010 (1)	0.0007 (1)	0.0053 (7)	0.0001 (3)	0.0019 (8)	−0.0002 (2)
N_4	0.008 (1)	0.0009 (1)	0.0056 (8)	−0.0001 (3)	0.0012 (8)	−0.0001 (2)
N_5	0.012 (1)	0.0009 (1)	0.0068 (8)	−0.0007 (3)	0.0019 (9)	−0.0001 (2)
N_6	0.009 (1)	0.0011 (1)	0.0080 (8)	−0.0006 (3)	0.0009 (9)	0.0004 (3)
O_1	0.017 (1)	0.0015 (1)	0.0083 (7)	−0.0020 (3)	0.0044 (8)	−0.0019 (2)
O_2	0.013 (1)	0.0012 (1)	0.0086 (7)	−0.0018 (3)	0.0039 (8)	−0.0014 (2)
C_1	0.011 (2)	0.0009 (1)	0.0069 (9)	−0.0001 (4)	0.001 (1)	0.0001 (3)
C_2	0.012 (2)	0.0012 (1)	0.008 (1)	−0.0007 (4)	0.001 (1)	0.0007 (3)
C_3	0.013 (2)	0.0010 (2)	0.008 (1)	−0.0003 (5)	0.003 (1)	0.0008 (3)
C_4	0.013 (2)	0.0011 (1)	0.007 (1)	0.0004 (5)	0.004 (1)	0.0001 (3)
C_5	0.013 (2)	0.0012 (1)	0.007 (1)	−0.0001 (4)	0.002 (1)	−0.0002 (3)
C_6	0.015 (2)	0.0018 (2)	0.011 (8)	−0.0011 (5)	0.005 (1)	−0.0019 (4)
C_7	0.016 (2)	0.0024 (2)	0.007 (1)	−0.0011 (5)	0.003 (1)	−0.0014 (3)
C_8	0.010 (2)	0.0008 (1)	0.007 (1)	−0.0002 (4)	0.003 (1)	−0.0004 (3)
C_9	0.008 (2)	0.0007 (1)	0.006 (1)	0.0003 (4)	0.001 (1)	−0.0002 (3)
C_{10}	0.070 (1)	0.0010 (1)	0.006 (1)	−0.0004 (4)	0.001 (1)	−0.0001 (3)
C_{11}	0.006 (1)	0.0009 (1)	0.006 (1)	−0.0002 (4)	0.002 (1)	−0.0002 (3)
C_{12}	0.006 (1)	0.0007 (1)	0.006 (1)	−0.0001 (4)	−0.001 (1)	−0.0001 (3)
C_{13}	0.007 (2)	0.0008 (1)	0.007 (1)	−0.0001 (4)	0.001 (1)	−0.0001 (3)
C_{14}	0.016 (2)	0.0014 (2)	0.009 (1)	−0.0033 (5)	0.003 (1)	−0.0008 (4)
C_{15}	0.019 (2)	0.0009 (2)	0.009 (1)	−0.0010 (5)	0.004 (1)	−0.0001 (3)
C_{16}	0.009 (2)	0.0012 (2)	0.008 (1)	−0.0004 (4)	0.001 (1)	0.0008 (3)
C_{17}	0.013 (2)	0.0015 (2)	0.015 (1)	−0.0016 (5)	0.004 (1)	0.0005 (4)
C_{18}	0.008 (2)	0.0021 (2)	0.016 (2)	−0.0010 (5)	0.004 (1)	0.0012 (5)
C_{19}	0.013 (2)	0.0013 (2)	0.011 (1)	−0.0001 (5)	0.004 (1)	0.0009 (4)
C_{20}	0.012 (2)	0.0015 (2)	0.008 (1)	−0.0001 (5)	0.003 (1)	0.0006 (4)

[a] Numbers in parentheses in all tables are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Hydrogen Atom Thermal Parameters

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
H_1[a]	2.61	H_8	4.30	H_{14}	3.72
H_2	3.19	H_9	3.58	H_{15}	4.48
H_3	3.14	H_{10}	2.23	H_{16}	4.63
H_4	3.10	H_{11}	3.79	H_{17}	3.90
H_5	4.20	H_{12}	3.79	H_{18}	3.53
H_6	4.20	H_{13}	3.72	H_{19}	3.53
H_7	4.30				

[a] The hydrogen atoms are numbered consecutively with H_1 attached to C_1. H_{19} is bonded to the oxygens. The thermal parameters were set to one unit greater than the isotopic thermal parameter of the atom to which it is attached.

Magnetic Measurements. Susceptibility measurements on a polycrystalline sample of the complex for which the structure was determined were made in the temperature range 80–302°K by the Faraday method using an Alpha Model 1402 complete susceptibility system with an Alpha Model 1424 variable-temperature accessory. In the temperature range 4.8–140°K, a Foner-type vibrating sample magnetometer[11] was used. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard[12] using an overlapping method to relate the magnetometer data to that calculated in the higher temperature region. Corrections for the diamagnetism of the substituent atoms, estimated from Pascal's constants,[13] were made for the sample.

Discussion

The structure of Cu_2LCl_3 consists of infinite chains of a bimetallic complex linked through single chloride bridges. See Figure 4. Thus the copper ions are not only connected *via* the pyrazine ligand but also *via* chloride bridges. Except for the copper-chloride bond distances the complex is essentially symmetrical. Although the ligand loses only one proton upon coordination, the symmetry is maintained through a resonance form of the ligand. The coordination around both copper atoms (Figure 5) is approximately trigonal bipyramidal with the pyrazine and pyridine nitrogens occupying the apical positions. The equatorial positions are occupied by the deprotonated amide nitrogen and two chlorides, one of which is the bridging chloride. Although the angles around copper in both equatorial planes are similar, the bond distances of copper to chloride are slightly different. The chloride distances to Cu_1 are essentially equal, 2.384 and 2.363 Å, while the chloride distances to Cu_2 are 2.239 and 2.622 Å (bridging chloride). The Cu_1-Cl-Cu_2 angle, 106.9°, is similar to those found in other copper-chlorine bridged structures. Table I lists the atomic parameters and Table II the thermal parameters for the atoms in the structure. Table III gives the H atom thermal parameters while Table IV lists bond distances in the structure and Table V the bond angles.

The X-ray structure leads to the formulation of the complex as in Figure 2. It is clear that the amide nitrogens are sp^2 hybridized as the sum of the angles around N_2 is 359.7° and N_5 is 359.6°. The O_1-O_2 distance of 2.48 Å is too short for bare carbonyl van der Waals interaction but fits for a O-H· · ·O system. Thus a rather unusual tautomerization takes place leading to the complex as described in Figure 2. The bond distances are also consistent with this formulation. (We thank a referee for pointing out this formulation.)

As had been reported previously, the magnetic susceptibility data for Cu_2LCl_3 obey the Curie-Weiss law, $\chi = C/(T + \Theta)$, over a wide range of temperatures. The Curie constant is calculated to be 0.453 with $\Theta = 1.5°$. Calculating from the equation $\mu_{\text{eff}} = 2.828C^{1/2}$, the magnetic moment is found to

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Table IV. Bond Distances (A)

Cu_1-Cl_1	2.363 (3)	Cu_2-Cl_1	2.622 (4)
Cu_1-Cl_3	2.384 (4)	Cu_2-Cl_2	2.239 (4)
Cu_1-N_1	2.006 (7)	Cu_2-N_6	1.996 (7)
Cu_1-N_2	1.956 (7)	Cu_2-N_5	1.954 (7)
Cu_1-N_3	2.055 (7)	Cu_2-N_4	2.022 (7)
N_1-C_1	1.34 (1)	N_6-C_{20}	1.33 (1)
N_1-C_5	1.34 (1)	N_6-C_{16}	1.35 (1)
N_2-C_7	1.47 (1)	N_5-C_{14}	1.47 (1)
N_2-C_8	1.26 (1)	N_5-C_{13}	1.29 (1)
N_3-C_9	1.35 (1)	N_4-C_{12}	1.35 (1)
N_3-C_{10}	1.31 (1)	N_4-C_{11}	1.32 (1)
C_1-C_2	1.37 (1)	$C_{19}-C_{20}$	1.36 (1)
C_2-C_3	1.38 (1)	$C_{18}-C_{19}$	1.38 (1)
C_3-C_4	1.37 (1)	$C_{17}-C_{18}$	1.38 (1)
C_4-C_5	1.38 (1)	$C_{16}-C_{17}$	1.39 (1)
C_5-C_6	1.53 (1)	$C_{15}-C_{16}$	1.50 (1)
C_6-C_7	1.47 (1)	$C_{14}-C_{15}$	1.51 (1)
C_8-O_1	1.29 (1)	$C_{13}-O_2$	1.27 (1)
C_8-C_9	1.50 (1)	$C_{12}-C_{13}$	1.50 (1)
$C_{10}-C_{11}$	1.38 (1)	O_1-H_{19}	1.31
		O_2-H_{19}	1.07

be 1.90 BM. It should be noted that this value is slightly higher than that which had been reported. This moment is reasonable considering the actual copper atoms' environments which have been determined since it has been shown theoretically[14] that the moment for a truly trigonal-bipyramidal copper(II) complex should be slightly greater than 2 BM. Unlike the first determination, however, this study shows more clearly that the Curie-Weiss law apparently fails at the lower temperature limit. As is displayed in Figure 6, this deviation in behavior is seen at temperatures lower than approximately 12°K. This effect is reflected in the experimental magnetic moment as well, since it appears to be temperature independent above 12°K but falls to 1.6 BM at 4.8°K. Such behavior can certainly be considered to be suggestive of weak antiferromagnetism.

Considering the observation that the magnetic properties of this complex suggest the possibility of spin interaction between the metal ions involved, the determined structural arrangement is a particularly interesting one. Two possible pathways for exchange can be found. Evidence exists that pyrazine ring bridges such as that present in this structure can transmit antiferromagnetic interactions,[15,16] even though the metal ions are far removed from one another. It has been proposed that a mechanism which involves overlap of the π orbitals of the aromatic heterocyclic amine with metal antibonding orbitals may be operative to produce this effect. In complexes in which this pathway for interaction appears likely, however, the magnitude of the coupling is usually quite small.

The second pathway which can be defined involves a chloride linkage. In one of the two copper environments the third position in the trigonal plane is occupied by a chloride atom from an adjacent molecule with a Cu-Cl distance of 2.622 (4) Å. Halide bridges have been observed in other copper complexes,[17-19] but these have generally not been with a single bridge, such as found in this instance. Bauer, *et al.*,[20] recently reported, however, the structure of [Cu(tet b)]$_2$Cl(ClO$_4$)$_3$ which also contains trigonal-bipyramidal copper(II) and a single Cu-Cl-Cu linkage. Unlike the present complex whose Cu-Cl-Cu angle is 106.9°, the bridge in the former species is nearly linear, being 174.2°. Another complex with similar structural features is (DMSO)$_2$CuCl$_2$ whose magnetic properties have been determined. This complex, although a linear polymer, has been shown[21] to consist of distorted trigonal-bipyramidal units with a single chloride bridge between adjacent copper(II) ions as well. In this instance the bridging angle is 144.6°. The magnetic properties of (DMSO)$_2$CuCl$_3$ reflected clearly that there are antiferromagnetic interactions between the copper(II) ions, per-

Table V. Bond Angles (deg)

$Cl_1-Cu_1-Cl_3$	106.4 (1)	$Cl_1-Cu_2-Cl_2$	103.0 (1)
$Cl_1-Cu_1-N_1$	91.8 (2)	$Cl_2-Cu_2-N_6$	93.3 (2)
$Cl_3-Cu_1-N_1$	94.5 (2)	$Cl_1-Cu_2-N_6$	90.1 (2)
$Cl_1-Cu_1-N_2$	142.0 (2)	$Cl_2-Cu_2-N_5$	145.3 (2)
$Cl_3-Cu_1-N_2$	110.2 (2)	$Cl_1-Cu_2-N_5$	110.5 (2)
$Cl_1-Cu_1-N_3$	89.2 (2)	$Cl_2-Cu_2-N_4$	94.3 (2)
$Cl_3-Cu_1-N_3$	94.7 (2)	$Cl_1-Cu_2-N_4$	86.7 (2)
$N_1-Cu_1-N_2$	95.0 (3)	$N_6-Cu_2-N_5$	95.0 (3)
$N_1-Cu_1-N_3$	170.0 (3)	$N_6-Cu_2-N_4$	172.2 (3)
$N_2-Cu_1-N_3$	78.2 (3)	$N_5-Cu_2-N_4$	79.5 (3)
$Cu_1-Cl_1-Cu_2$	106.9 (1)	$Cu_2-N_6-C_{20}$	118.0 (6)
$Cu_1-N_1-C_1$	115.5 (6)	$Cu_2-N_6-C_{16}$	122.1 (6)
$Cu_1-N_1-C_5$	126.5 (6)	$C_{16}-N_6-C_{20}$	119.8 (8)
$C_1-N_1-C_5$	117.9 (8)	$Cu_2-N_5-C_{14}$	123.8 (6)
$Cu_1-N_2-C_7$	120.6 (6)	$Cu_2-N_5-C_{13}$	118.4 (6)
$Cu_1-N_2-C_8$	119.9 (6)	$C_{13}-N_5-C_{14}$	117.4 (8)
$C_7-N_2-C_8$	119.2 (8)	$Cu_2-N_4-C_{12}$	115.5 (8)
$Cu_1-N_3-C_9$	115.2 (6)	$Cu_2-N_4-C_{11}$	124.1 (8)
$Cu_1-N_3-C_{10}$	124.8 (6)	$C_{11}-N_4-C_{12}$	120.3 (8)
$C_9-N_3-C_{10}$	119.9 (8)	$N_6-C_{20}-C_{19}$	123.1 (9)
$N_1-C_1-C_2$	122.3 (9)	$N_6-C_{20}-H_{18}$	118.2 (8)
$N_1-C_1-H_1$	118.9 (9)	$C_{19}-C_{20}-H_{18}$	118.6 (9)
$C_2-C_1-H_1$	118.8 (9)	$C_{18}-C_{19}-C_{20}$	118.8 (9)
$C_1-C_2-C_3$	119.6 (9)	$C_{18}-C_{19}-H_{17}$	119.6 (9)
$C_1-C_2-H_2$	120.3 (9)	$C_{20}-C_{19}-H_{17}$	121.6 (10)
$C_3-C_2-H_2$	120.0 (9)	$C_{17}-C_{18}-C_{19}$	118.4 (9)
$C_2-C_3-C_4$	118.0 (9)	$C_{17}-C_{18}-H_{16}$	120.4 (10)
$C_2-C_3-H_3$	121.4 (9)	$C_3-O_1-H_{19}$	112.9 (9)
$C_4-C_3-H_3$	120.6 (9)	$C_{13}-O_2-H_{19}$	115.2 (9)
$C_3-C_4-C_5$	119.7 (9)	$C_{19}-C_{18}-H_{16}$	121.1 (10)
$C_3-C_4-H_4$	119.9 (9)	$C_{16}-C_{17}-C_{18}$	120.3 (10)
$C_5-C_4-H_4$	120.5 (9)	$C_{16}-C_{17}-H_{15}$	119.3 (10)
$N_1-C_5-C_4$	122.4 (9)	$C_{18}-C_{17}-H_{15}$	120.4 (9)
$N_1-C_5-C_6$	118.8 (9)	$N_6-C_{16}-C_{15}$	119.8 (8)
$C_4-C_5-C_6$	118.6 (9)	$N_6-C_{16}-C_{17}$	119.4 (9)
$C_5-C_6-C_7$	116.6 (9)	$C_{15}-C_{16}-C_{17}$	120.8 (9)
$C_5-C_6-H_5$	109.8 (9)	$C_{14}-C_{15}-C_{16}$	114.9 (8)
$C_7-C_6-H_5$	109.6 (9)	$C_{14}-C_{15}-H_{13}$	108.9 (8)
$C_5-C_6-H_6$	108.0 (9)	$C_{16}-C_{15}-H_{13}$	107.9 (8)
$C_7-C_6-H_6$	106.0 (9)	$C_{14}-C_{15}-H$	109.5 (8)
$H_5-C_6-H_6$	106.3 (9)	$C_{16}-C_{15}-H_{14}$	107.6 (8)
$N_2-C_7-C_6$	111.3 (9)	$H_{13}-C_{15}-H_{14}$	107.7 (8)
$N_2-C_7-H_7$	109.8 (9)	$N_5-C_{14}-C_{15}$	110.5 (9)
$N_2-C_7-H_8$	110.5 (9)	$N_5-C_{14}-H_{11}$	109.5 (9)
$C_6-C_7-H_7$	108.0 (9)	$N_5-C_{14}-H_{12}$	109.5 (9)
$C_6-C_7-H_8$	111.2 (9)	$C_{15}-C_{14}-H_{11}$	109.9 (9)
$H_7-C_7-H_8$	105.8 (9)	$C_{15}-C_{14}-H_{12}$	109.4 (9)
$N_2-C_8-O_1$	124.8 (9)	$H_{11}-C_{14}-H_{12}$	107.9 (9)
$N_2-C_8-C_9$	114.8 (9)	$N_5-C_{13}-O_2$	125.0 (9)
$O_1-C_8-C_9$	120.3 (9)	$N_5-C_{13}-C_{12}$	114.7 (9)
$N_3-C_9-C_8$	111.7 (9)	$O_2-C_{13}-C_{12}$	120.3 (9)
$N_3-C_9-C_{12}$	119.4 (9)	$N_4-C_{12}-C_{13}$	111.7 (9)
$C_8-C_9-C_{12}$	128.9 (9)	$N_4-C_{12}-C_9$	119.4 (9)
$N_3-C_{10}-C_{11}$	121.2 (9)	$C_9-C_{12}-C_{13}$	128.9 (9)
$N_3-C_{10}-H_9$	119.2 (9)	$N_4-C_{11}-C_{10}$	119.6 (9)
$C_{11}-C_{10}-H_9$	119.6 (9)	$N_4-C_{11}-H_{10}$	119.8 (9)
		$C_{10}-C_{11}-H_{10}$	120.6 (9)

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haps in the manner of an infinite chain.[22] The significant parameters reported were $2J = -9.6$ cm^{-1} and $g = 2.22$.

Thus, although the magnitude of the interaction in Cu_2LCl_3 could only be of the order of two wave numbers, it appears that there are two possible and reasonable bridging routes over which such a coupling could occur. Unhappily, it appears impossible in this case to distinguish which or possibly if both are operable. Studies on similar complexes are continuing in an effort to resolve this difficulty.[23]

Registry No. Cu_2LCl_3, 50859-34-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies if the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1042.

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Structure of a Stable π-Arene–Chromium Dicarbonyl Complex with Bis(diphenylarsino)methane

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The crystal and molecular structure of a stable π-arene–chromium dicarbonyl complex of bis(diphenylarsino)methane (DAM) $[\{(\pi\text{-}C_6H_5)(C_6H_5)AsCH_2As(C_6H_5)_2\}Cr(CO)_2]$ has been determined by three-dimensional X-ray structural analysis, using data collected by counter methods. The complex crystallizes in the space group $P\bar{1}$ (C_i^1, No. 2), $a = 7.609$ (3), $b = 8.563$ (3), $c = 18.677$ (5) Å, $\alpha = 83.16$ (2), $\beta = 82.52$ (2), $\gamma = 81.66$ (2)°, $Z = 2$. The measured and calculated densities of 1.62 (1) and 1.622 g cm^{-3}, respectively, are in excellent agreement. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods to final weighted and unweighted reliability indices of 0.042 and 0.032, respectively, for the 3208 independent reflections for which $I/\sigma(I) \geqslant 3.0$. One As atom is disordered, and the populations of the two possible positions have been successfully refined to 0.9510 (9) and 0.0582 (9). The coordination at the central chromium atom is essentially octahedral, with the two carbonyl groups and one σ-bonded As atom of the DAM ligand occupying three mutually cis coordination sites. The remaining sites at the chromium atom are occupied by a delocalized π-arene ring which is also bonded to the second As atom of the DAM ligand. Although the Cr–C(arene) distances vary from 2.165 (4) to 2.194 (4) Å, the Cr–π-arene bonding appears to be essentially symmetric. The shortest distances are approximately trans to the σ-bonded arsenic atom. The π-arene ring is planar within experimental error, and there is no systematic alternation of C–C bond distances within this ring.

Introduction

π-Arene–chromium tricarbonyl complexes of the form $[(\pi\text{-arene})Cr(CO)_3]$ are readily formed by the reaction of $Cr(CO)_6$ with benzenoid compounds. The preparative and structural aspects of much of this chemistry have been reviewed in recent years.[1-3] Without doubt, the best known and most widely studied of the π-arene–chromium complexes is dibenzenechromium. Early structural data for this molecule[4] suggested a marked threefold distortion of the arene groups, with alternating carbon–carbon distances of 1.353 and 1.439 Å. However, later work cast some doubt on this result[5-7] with, in particular, gas-phase electron diffraction studies indicating that the carbon–carbon bond length differences could not exceed 0.02 Å.[7] The situation regarding the solid state was resolved only by a careful reinvestigation of the structure at low temperature (100°K) which indicated that the carbon–carbon distances are, in fact, all equal to within 0.001 Å.[8] A systematic investigation of the supposed threefold distortion was also carried out by Dahl and Bailey who determined the structure of (π-hexamethylbenzene)chromium tricarbonyl[9] and reinvestigated the structure of (π-benzene)chromium tricarbonyl.[10-13] No systematic distortion was observed. However, a recent and very precise investigation of the structure of $(\pi\text{-}C_6H_6)Cr(CO)_3$ at 78°K,[14] using both X-ray and neutron diffraction methods, has unequivocally established the presence of the expected threefold distortion. The bond length alternation is small ($\Delta_{av} = 0.018$ (2) Å) but is statistically highly significant ($\Delta/\sigma \doteq 9$). In each of these derivatives, the Cr–CO bonds are directed toward the midpoints of the C–C bonds of the π-arene ring, giving the staggered configuration I.

A series of related structures, with mono- and disubstituted benzenoids, has been reported by Sim, *et al.*,[15-18] who found

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