

ride, Cl(2). The oxygen atom of water 1 is bound to an amine hydrogen atom N(3)H(2) of a complex ion related to the first by a center of symmetry. The second chloride, Cl(2), is bound to an amine hydrogen atom, N(1)H(2), of the complex and to two amine hydrogen atoms, N(1)H(1) and N(2)H(2), of two ligands of another centrosymmetrically related complex. Thus five of the amine hydrogen atoms of a single complex are bound to chloride ions, while the sixth is bound to the oxygen atom of a water of crystallization.

Hydrogen bonding between amine donor atoms and water has also been observed in $[\text{Fe}^{\text{III}}(\text{sal})_2\text{trien}]\text{Cl}\cdot 2\text{H}_2\text{O}$ and $[\text{Fe}^{\text{III}}(\text{sal})_2\text{trien}]\text{NO}_3\cdot \text{H}_2\text{O}$,⁵ both of which exhibit chain hydrogen-bonding networks. The fact that both compounds are low spin at room temperature has been attributed to the strong NH-O hydrogen-bonding interactions favoring the low-spin state. Greenaway and Sinn,⁸ in their room-temperature investigations of low-spin *fac*- $\text{Fe}(\text{2-pic})_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$ and high-spin *mer*- $\text{Fe}(\text{2-pic})_3\text{Cl}_2\cdot \text{CH}_3\text{OH}$, suggest that the difference in room-temperature spin states can be attributed to the presence of a NH-O interaction in the former but not in the latter. (In both these compounds all amine hydrogen atoms not involved in hydrogen bonding to oxygen atoms do exhibit interactions with the chloride ions.) While the *fac* complex in the dihydrate, which is low spin both at 115 K and at room temperature, exhibits an NH-O interaction, the *fac* isomer of the diiodide, which is predominantly low spin at room temperature,

has no such interaction. The *mer* isomer of the diiodide and the *mer* complexes in the methanol and ethanol solvates of the dichloride all lack NH-O interactions and are all high spin at room temperature. These results suggest that the room-temperature spin state in tris(2-picolylamine)iron(II) complexes is influenced more strongly by the complex geometry than by the hydrogen bonding. The comparison of iron-amine and iron-pyridine bond distances presented above supports the hypothesis that the *fac* geometry stabilizes the low-spin electronic configuration.

Acknowledgment. This work was supported by the UCLA research committee, the UCLA office of Academic Computing, and the National Science Foundation (Grant CHE78-01564). Bradley A. Katz was supported by a UCLA chancellor's fellowship and Charles E. Strouse acknowledges the support of an Alfred P. Sloan research fellowship.

Registry No. *fac*- $\text{Fe}(\text{2-pic})_3\text{I}_2$, 72228-92-3; *mer*- $\text{Fe}(\text{2-pic})_3\text{I}_2$, 72244-68-9; *fac*- $\text{Fe}(\text{2-pic})_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$, 68889-84-9.

Supplementary Material Available: A listing of atomic positional and thermal parameters at room temperature for the dihydrate, a table of bond distances and angles at room temperature for the dihydrate, a table of hydrogen-bonding interactions for the dihydrate, and a listing of observed and calculated structure factors for the dihydrate at 115 K and at room temperature and for the diiodide at room temperature (44 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination du CNRS, Associé à l'Université Paul Sabatier, 31400 Toulouse, France

Synthesis and Crystal and Molecular Structure of the 2:1 Molecular Adduct between *N,N'*-(1,2-Phenylene)bis(salicylaldiminato)copper(II) and 7,7,8,8-Tetracyanoquinodimethane

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Received July 11, 1979

A molecular adduct (2:1) between a tetradentate Schiff base complex, *N,N'*-(1,2-phenylene)bis(salicylaldiminato)copper(II) [$\text{Cu}(\text{salphen})$], and 7,7,8,8-tetracyanoquinodimethane (TCNQ) is described. The conditions necessary to obtain this adduct are very critical, and the solution electronic spectra of the mixed component molecules show a new band at $\sim 4300 \text{ \AA}$, with respect to the spectra of the starting materials, only several hours after mixing. This adduct crystallizes in the triclinic system, space group $P\bar{1}$, with cell constants $a = 11.970(4) \text{ \AA}$, $b = 12.567(4) \text{ \AA}$, $c = 7.020(2) \text{ \AA}$, $\alpha = 103.44(2)^\circ$, $\beta = 92.35(2)^\circ$, and $\gamma = 92.48(2)^\circ$. Least-squares refinement of the structure led to a final R factor (F basis) of 0.039 ($R_w = 0.040$) using 2384 independent reflections. The structure consists of stacks of centrosymmetrically related, nearly planar $\text{Cu}(\text{salphen})$ molecules, running in the c direction parallel to stacks of TCNQ molecules, whose spacing is twice that of the $\text{Cu}(\text{salphen})$ units. The geometry of the TCNQ molecule suggests the degree of charge transfer to be quite weak. Magnetic measurements from 9 to 295 K and the 77 K ESR spectrum show that there is no strong coupling between $\text{Cu}(\text{II})$ ions. The electrical conductivity, measured on a pressed powder at room temperature, $\sigma = 10^{-8} \Omega^{-1} \text{ cm}^{-1}$, is 10 to 100 times higher than that of the starting materials. The overlapping of molecules of $\text{Cu}(\text{salphen})$ with molecules of TCNQ in the solid state is discussed.

Introduction

Molecular "charge transfer" or donor-acceptor adducts between various organic electron donors and acceptors have been known for many years and widely studied.¹⁻³ On the other hand, there are much fewer examples of charge-transfer complexes that are composed of transition-metal complexes and organic acceptors⁴⁻¹⁰ or donors.¹¹⁻¹⁵ Both the strictly

organic (i.e., the tetrathiafulvalene-tetracyanoquinodimethane-like compounds¹⁶) and the transition-metal complex

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systems have received considerable attention in the past decade because of their unusual optical, magnetic, and electrical properties.

For both types of compounds, the degree of charge transfer between the donor and acceptor is believed to be an important factor in determining the crystal structure and physical properties of the adduct. In the metal complex case, donor-acceptor adducts are known in which there is essentially complete, one-electron charge transfer^{6,13-15} in the ground state yielding ionic solids or negligible charge transfer with the molecule present in their neutral forms.⁹ The intermediate situation, involving a partial (less than one electron) charge transfer, has also been found.^{5,17-19}

The examples of charge-transfer adducts of transition-metal chelates and organic molecules include (i) the adducts between bis(8-hydroxyquinolato)metal(II) and tetracyanoquinodimethane,^{4,17,18} (ii) metal bis(dithiolene) complexes with various organic donors¹¹⁻¹⁵ or acceptors,⁶ and (iii) some Schiff base-metal complexes with acceptors such as 1,3,5-trinitrobenzene.^{7,19} Nishida et al.²⁰ have recently reported that no molecular adduct could be obtained between a copper(II) complex of a tetradentate Schiff base ligand and the powerful electron-acceptor tetracyanoquinodimethane.

In this paper, we report the preparation and crystal and molecular structure of the first molecular adduct (2:1) between a tetradentate Schiff base complex, *N,N'*-(1,2-phenylene)-bis(salicylaldiminato)copper(II) [Cu(salphen)], and 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Experimental Section

Synthesis. *N,N'*-(1,2-Phenylene)bis(salicylaldiminato)copper(II) [Cu(salphen)] was prepared (i) as prescribed by Pfeiffer et al.,²¹ by reaction of 1,2-phenylenediamine with bis(salicylaldehyde)copper(II), or (ii) by direct action of copper acetate on the tetradentate Schiff base *N,N'*-(1,2-phenylene)salicylaldimine (salphen) in ethanol and recrystallized from chloroform. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was purchased from Aldrich-Europe.

A solution of 0.3779 g (1 mmol) of Cu(salphen) in 125 mL of chloroform was added, at room temperature, to a solution of 0.2042 g (1 mmol) of TCNQ in 75 mL of acetonitrile. Very slow evaporation, under a definite procedure (given later), yielded tiny blue-black shiny crystals which were filtered off and dried under vacuum (0.4312 g, 74%). Quantitative analysis (by the Service Central de Microanalyse du CNRS) gave results corresponding to a 2:1 stoichiometry. Anal. Calcd for [Cu(C₂₀H₁₄N₂O₂)₂·(C₁₂H₄N₄)]: C, 65.06; H, 3.36; N, 11.67; Cu, 13.24. Found: C, 65.09; H, 3.85; N, 11.77; Cu 13.13. The 2:1 stoichiometry was later confirmed by the X-ray structure determination.

No other adduct with different stoichiometries could be obtained by warming the solutions and varying the molecular ratio of the starting materials.

The conditions of crystallization were very critical. Fast evaporation of the chloroform-acetonitrile solutions yielded the uncomplexed starting materials. Slow air evaporation gave a poor yield of the 2:1 adduct mixed with a greenish powder. Slow addition or diffusion of ether into the chloroform-acetonitrile solution yielded brown needles. The X-ray powder pattern of these needles shows that they are different from either the starting materials or the 2:1 adduct.

The best procedure for obtaining the 2:1 adduct is a very slow evaporation (about 3 weeks) of the chloroform-acetonitrile solution, under inert atmosphere, through a controlled reduced pressure (400–600 torr). No solvent other than chloroform and acetonitrile

Table I. Experimental Crystallographic Data

(1) Physical and Crystallographic Data	
formula:	mol wt: 959.978
[Cu(C ₂₀ H ₁₄ N ₂ O ₂) ₂ ·(C ₁₂ H ₄ N ₄)	<i>V</i> = 1025 Å ³
crystal system: triclinic	<i>Z</i> = 1
space group: <i>P</i> 1̄	ρ_{exptl} was not measured
<i>a</i> = 11.970 (4) Å	$\rho_x = 1.555 \text{ g/cm}^3$
<i>b</i> = 12.567 (4) Å	abs factor: $\mu_{\text{MoK}\alpha} =$
<i>c</i> = 7.020 (2) Å	10.98 cm ⁻¹
$\alpha = 103.44 (2)^\circ$	morphology: spheroidal, $\phi =$
$\beta = 92.35 (2)^\circ$	0.025 cm
$\gamma = 92.48 (2)^\circ$	

(2) Data Collection

temp: 293 K
 radiation: $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$
 crystal-detector distance: 208 mm
 detector window: height = 4 mm; width = 3 mm
 takeoff angle: 2.25°
 scan mode: ω scan
 max Bragg angle: 26°
 scan angle: $\Delta\theta = \Delta\theta_0 + B \tan \theta$, $\Delta\theta_0^a = 1.2^\circ$, $B^a = 0.347$
 values determining the scan speed: $\text{SIGPRE}^a = 0.66$; $\text{SIGMA}^a = 0.018$; $\text{VPRE}^a = 10^\circ/\text{min}$; $\text{TMAX}^a = 80 \text{ s}$
 test refltns: intens, 421, 122, 042 measd every 3600 s;
 orientation, 233, 740, 500 controlled every 100 refltns

^a These parameters have been described in: Mosset, A.; Bonnet, J. J.; Galy, J. *Acta Crystallogr., Sect. B* 1977, 33, 2633.

proved to be as suitable. Large crystals of the so obtained 2:1 adduct could not be grown. Although the X-ray analysis shows that single crystals were obtained, they rather look like small ($0.2 \times 0.1 \times 0.1 \text{ mm}^3$) chips of glass with no definite faces. They are air stable and do not melt at temperatures as high as 350°C .

Physical Measurements. Visible and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 577 spectrophotometer.

Molecular weight determinations were carried out by osmometry in methyl ethyl ketone, using a Mechrolab osmometer.

Powder conductivities were estimated on compressed pellets with a Keithley Model 225 current source and a Keithley Model 616 electrometer. The pellets were pressed and their resistance was measured directly in a "conductivity press" by applying a force of 700 kg on 3-mm diameter pistons moving in a glass capillary tube.

The magnetic measurements were carried out with a Faraday-type magnetometer, equipped with a continuous flow cryostat designed by Oxford Instruments, over the temperature range 8.9–295 K. Mercury tetrathiocyanatocobaltate(II) was used as a susceptibility standard.

ESR spectra were recorded at X-band frequencies on a Varian E-9 spectrometer at 77 K. The magnetic field was swept from 0 to over 8 kG and calibrated with a digital NMR gaussmeter.

A Guinier-de Wolf camera utilizing monochromatized copper radiation was used for X-ray powder patterns.

Single-Crystal X-ray Data Collection. Photographs taken with a single crystal placed on a Stoe precession camera, using Mo $K\alpha$ radiation, showed that the complex crystallizes in the triclinic system. The same crystal was mounted on an Enraf-Nonius CAD-4 computer-controlled four-circle diffractometer. Accurate unit-cell constants were derived from a least-squares refinement of the setting angles of 25 reflections (Table I).

Intensity measurements were made for the forms *hkl*, $\bar{h}kl$, *h* $\bar{k}$ *l*, and $\bar{h}\bar{k}l$. Reflections with $2\theta \leq 52^\circ$ were scanned as described in Table I, using graphite-monochromatized Mo $K\alpha$ radiation. The data were processed²² by using an ignorance factor *p* of 0.02 in the estimation of standard deviations. No absorption corrections were applied since the small value of the linear absorption coefficient, $\mu = 10.981 \text{ cm}^{-1}$, combined with the roughly spherical shape of the selected crystal yielded a nearly isotropic $\mu R = 0.13$. Among the 4028 independent

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Table II. Positional and Thermal Parameters for the Atoms of [Cu(salphen)]₂·TCNQ

ATOM	X	Y	Z	B11 OR B(Å ²) B22	B33	B12	B13	B23
Cu	0.19055(4)	0.35186(5)	0.03867(8)	37.8(4)	41.3(4)	160.5(15)	5.09(26)	14.6(5)
O(1)	0.34358(22)	0.37870(23)	0.0005(4)	44.1(23)	50.1(25)	280.(9)	1.8(20)	1.8(20)
O(2)	0.18903(22)	0.49649(23)	0.1977(4)	38.2(22)	49.3(24)	216.(8)	4.7(18)	12.(3)
N(1)	0.18778(26)	0.19968(26)	-0.1074(5)	44.6(26)	39.1(27)	134.(8)	5.5(22)	4.(4)
N(2)	0.03301(25)	0.31914(25)	0.0656(4)	41.1(25)	34.7(26)	131.(8)	3.6(21)	10.(4)
N(1)T	0.3045(4)	0.1617(4)	0.3305(7)	82.(4)	82.(4)	340.(14)	-29.(3)	14.(6)
N(2)T	0.6660(4)	0.1647(3)	0.2772(7)	88.(4)	73.(4)	352.(14)	13.(3)	52.(6)
C(1)	0.2754(3)	0.1479(4)	-0.1706(6)	60.(3)	46.(3)	165.(11)	13.5(28)	17.(5)
C(2)	-0.0368(3)	0.3903(3)	0.1445(6)	34.4(28)	49.(3)	141.(10)	3.6(25)	14.(4)
C(1)T	0.3956(3)	0.4424(4)	0.4806(6)	38.(3)	58.(4)	209.(12)	-5.4(27)	5.(5)
C(2)T	0.5997(3)	0.4487(4)	0.4552(6)	41.(3)	56.(4)	213.(12)	-1.1(28)	5.(5)
C(3)T	0.4954(3)	0.3848(3)	0.4322(6)	52.(3)	52.(3)	130.(10)	-4.1(27)	-4.(5)
C(4)T	0.4917(3)	0.2736(4)	0.3649(6)	49.(3)	53.(4)	137.(10)	-1.9(27)	4.(4)
C(5)T	0.3876(4)	0.2091(4)	0.3432(7)	73.(4)	56.(4)	177.(12)	-3.(3)	7.(6)
C(6)T	0.5891(4)	0.2131(4)	0.3147(7)	67.(4)	55.(4)	208.(13)	-7.(3)	12.(6)
C(1)G1	0.4701(4)	0.1239(4)	-0.2360(7)	4.19(10)				
C(2)G1	0.5789(4)	0.1634(4)	-0.2350(7)	4.46(10)				
C(3)G1	0.6066(4)	0.2727(4)	-0.1590(7)	4.03(10)				
C(4)G1	0.5272(3)	0.3439(4)	-0.0828(6)	3.45(9)				
C(5)G1	0.4137(3)	0.3071(4)	-0.0789(6)	2.99(8)				
C(6)G1	0.3861(3)	0.1954(4)	-0.1580(6)	2.93(8)				
C(1)G2	0.1196(3)	0.6552(3)	0.3848(6)	2.83(8)				
C(2)G2	0.0315(3)	0.7144(4)	0.4620(6)	3.35(9)				
C(3)G2	-0.0777(3)	0.6700(3)	0.4315(6)	3.12(8)				
C(4)G2	-0.0975(3)	0.5644(3)	0.3251(6)	2.69(8)				
C(5)G2	-0.0084(3)	0.5005(3)	0.2459(6)	2.39(8)				
C(6)G2	0.1027(3)	0.5466(3)	0.2713(6)	2.56(8)				
C(1)G3	-0.1111(3)	0.1657(3)	-0.0327(6)	2.97(8)				
C(2)G3	-0.1380(4)	0.0602(4)	-0.1396(6)	3.49(9)				
C(3)G3	-0.0575(4)	-0.0003(4)	-0.2435(6)	3.71(9)				
C(4)G3	0.0505(3)	0.0417(3)	-0.2375(6)	3.17(8)				
C(5)G3	0.0799(3)	0.1470(3)	-0.1287(6)	2.52(7)				
C(6)G3	-0.0027(3)	0.2110(3)	-0.0306(5)	2.31(7)				
H(1)	0.264	0.072	-0.230	3.5				
H(2)	-0.114	0.366	0.135	3.5				
H(1)T	0.326	0.402	0.468	4.0				
H(2)T	0.667	0.412	0.425	4.0				
H(1)G1	0.450	0.048	-0.289	5.2				
H(2)G1	0.634	0.115	-0.288	5.5				
H(3)G1	0.682	0.300	-0.159	5.0				
H(4)G1	0.547	0.419	-0.030	4.4				
H(1)G2	0.194	0.687	0.405	3.8				
H(2)G2	0.046	0.788	0.536	4.4				
H(3)G2	-0.138	0.712	0.485	4.1				
H(4)G2	-0.172	0.533	0.305	3.7				
H(1)G3	-0.167	0.208	0.037	4.0				
H(2)G3	-0.212	0.030	-0.143	4.5				
H(3)G3	-0.076	-0.073	-0.317	4.7				
H(4)G3	0.106	-0.001	-0.307	4.2				

^a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

reflections collected, 2384 had $F_o^2 \geq 3\sigma(F_o^2)$ and were used to refine the structural parameters.

Structure Refinement. Refinement of the structure was effected by full-matrix least-squares techniques.²² Throughout the refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight w is $4F_o^2/\sigma^2(F_o^2)$. The reliability coefficients are defined as

$$R = \sum (||F_o| - |F_c||) / \sum F_o$$

$$R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$$

The atomic scattering factors for all atoms and anomalous terms for the copper atom are from the tabulation in ref 23.

The density of the crystals was not measured; however, the density calculated from the cell constants is given by $\rho = 1.555 \times Z$ (g/cm³), from which it would seem reasonable that $Z = 1$. Space group $P1$ was assumed; this implies the center of the TCNQ molecule to lie on a center of symmetry. This choice was confirmed as correct by the structure solution.

The copper atom was positioned from a Patterson map. The remaining nonhydrogen atoms were localized on two Fourier or difference Fourier maps in ensuing cycles of refinement. An isotropic refinement treating the Cu(salphen) phenyl groups as rigid bodies (C₆H₅) resulted in $R = 0.078$ and $R_w = 0.082$. Introducing anisotropic temperature factors for nongroup atoms yielded $R = 0.047$ and $R_w = 0.051$. The secondary extinction correction was relevant, and the introduction of the four missing nongroup hydrogen atoms as fixed contributions to F_c did not change significantly the agreement coefficients. At this stage of refinement, a close examination of a

difference Fourier map showed that most of the remaining peaks were located on the Cu(salphen) phenyl groups which had been refined as rigid bodies. This suggested that the rigid body approximation was not suitable. Consequently, two more cycles of refinement were run in which the atoms of phenyl groups were refined individually but isotropically. In these cycles the hydrogen atoms of phenyl groups were assigned fixed isotropic thermal coefficients 1 Å² higher than those of their binding C atoms, and C-H distances were kept equal to 0.95 Å. Convergence was achieved with $R = 0.039$ and $R_w = 0.040$ for the 2384 observations above background and 208 variables. It did not appear worthwhile from a financial point of view to go on refining the phenyl atoms anisotropically. In the last cycle of refinement, the shift per error was less than 0.1 for copper, oxygen, and nitrogen atoms and less than 0.3 for carbon atoms. The error in an observation of unit weight was 1.79 e. A final difference Fourier map did not exhibit peaks higher than $1/11$ of peaks corresponding to a carbon atom on a Fourier map.

A listing of observed and calculated structure amplitudes and the derived root-mean-square amplitudes of vibration are available as supplementary material. Refined atomic parameters are listed in Table II.

Results and Discussion

Formation Conditions of [Cu(salphen)]₂·TCNQ. The absorption spectra of mixtures of solutions of Cu(salphen) and TCNQ in acetone or acetonitrile were observed, initially and even after 24 h, to be a superposition of the spectra of the starting component molecules. This fact, indicating that no appreciable complex formation had occurred, was quantitatively confirmed by use of the continuous variation method.²⁴

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Table III. Bond lengths (Å) and Angles (Deg) in $[\text{Cu}(\text{salphen})]_2 \cdot \text{TCNQ}$

In $[\text{Cu}(\text{salphen})]$					
Cu-O(1)	1.890 (3)	O(1)-Cu-O(2)	88.8 (1)	O(2)-C(6)G2-C(5)G2	124.7 (3)
Cu-O(2)	1.900 (3)	N(1)-Cu-N(2)	83.8 (1)	C(2)-C(5)G2-C(6)G2	123.1 (4)
Cu-N(1)	1.947 (3)	O(1)-Cu-N(1)	93.7 (1)	N(2)-C(2)-C(5)G2	125.7 (3)
Cu-N(2)	1.939 (3)	O(2)-Cu-N(2)	93.8 (1)	Cu-N(2)-C(2)	124.8 (3)
O(1)-C(5)G1	1.302 (5)	O(1)-Cu-N(2)	177.2 (2)	O(2)-C(6)G2-C(1)G2	118.3 (3)
O(2)-C(6)G2	1.296 (5)	O(2)-Cu-N(1)	175.6 (2)	C(2)-C(5)G2-C(4)G2	116.8 (3)
N(1)-C(1)	1.298 (5)	Cu-O(1)-C(5)G1	127.0 (3)	Cu-N(2)-C(6)G3	113.0 (2)
N(2)-C(2)	1.295 (5)	O(1)-C(5)G1-C(6)G1	125.0 (4)	N(2)-C(6)G3-C(5)G3	115.5 (3)
N(1)-C(5)G3	1.411 (5)	C(1)-C(6)G1-C(5)G1	123.4 (4)	N(2)-C(6)G3-C(1)G3	124.9 (3)
N(2)-C(6)G3	1.409 (5)	N(1)-C(1)-C(6)G1	125.4 (4)	N(1)-C(5)G3-C(6)G3	114.5 (3)
C(1)-C(6)G1	1.420 (6)	Cu-N(1)-C(1)	124.8 (3)	N(1)-C(5)G3-C(4)G3	126.1 (3)
C(2)-C(5)G2	1.422 (5)	O(1)-C(5)G1-C(4)G1	117.8 (4)	Cu-N(1)-C(5)G3	113.0 (2)
		C(1)-C(1)G1-C(6)G1	116.3 (4)	C(2)-N(2)-C(6)G3	121.8 (3)
		Cu-O(2)-C(6)G2	127.2 (2)	C(1)-N(1)-C(5)G3	122.0 (3)
C(1)G1-C(2)G1	1.373 (7)	C(2)G1-C(1)G1-C(6)G1	120.3 (4)	C(4)G2-C(5)G2	1.417 (6)
C(2)G1-C(3)G1	1.373 (7)	C(3)G1-C(2)G1-C(1)G1	119.9 (4)	C(5)G2-C(6)G2	1.416 (6)
C(3)G1-C(4)G1	1.371 (6)	C(4)G1-C(3)G1-C(2)G1	121.2 (4)	C(6)G2-C(1)G2	1.413 (5)
C(4)G1-C(5)G1	1.420 (6)	C(5)G1-C(4)G1-C(3)G1	120.7 (4)	C(1)G3-C(2)G3	1.381 (6)
C(5)G1-C(6)G1	1.404 (6)	C(6)G1-C(5)G1-C(4)G1	117.3 (4)	C(2)G3-C(3)G3	1.380 (6)
C(6)G1-C(1)G1	1.418 (6)	C(1)G1-C(6)G1-C(5)G1	120.2 (4)	C(3)G3-C(4)G3	1.370 (6)
C(1)G2-C(2)G2	1.373 (6)	C(2)G2-C(1)G2-C(6)G2	121.4 (4)	C(4)G3-C(5)G3	1.387 (5)
C(2)G2-C(3)G2	1.387 (6)	C(3)G2-C(2)G2-C(1)G2	121.4 (4)	C(5)G3-C(6)G3	1.403 (5)
C(3)G2-C(4)G2	1.368 (5)	C(4)G2-C(3)G2-C(2)G2	119.2 (4)	C(6)G3-C(1)G3	1.391 (5)
				C(5)G2-C(4)G2-C(3)G2	120.9 (4)
				C(6)G2-C(5)G2-C(4)G2	120.1 (3)
				C(1)G2-C(6)G2-C(5)G2	117.0 (4)
				C(2)G3-C(1)G3-C(6)G3	119.9 (4)
				C(3)G3-C(2)G3-C(1)G3	120.0 (4)
				C(4)G3-C(3)G3-C(2)G3	120.8 (4)
				C(5)G3-C(4)G3-C(3)G3	120.2 (4)
				C(6)G3-C(5)G3-C(4)G3	119.3 (3)
				C(1)G3-C(6)G3-C(5)G3	119.6 (3)
In TCNQ					
C(1)T-C(2)T'	1.336 (6)	C(3)T-C(1)T-C(2)T'	120.8 (4)	C(4)T-C(6)T	1.431 (6)
C(1)T-C(3)T	1.435 (6)	C(3)T-C(2)T-T-C(1)T'	121.7 (4)	C(5)T-N(1)T	1.126 (6)
C(2)T-C(3)T	1.437 (6)	C(1)T-C(3)T-T-C(2)T	117.5 (4)	C(6)T-N(2)T	1.132 (6)
C(3)T-C(4)T	1.366 (6)	C(1)T-C(3)T-T-C(4)T	121.4 (4)		
C(4)T-C(5)T	1.439 (6)	C(2)T-C(3)T-T-C(4)T	121.0 (4)	C(3)T-C(4)T-T-C(5)T	121.3 (4)
				C(3)T-C(4)T-T-C(6)T	123.2 (4)
				C(5)T-C(4)T-T-C(6)T	115.5 (4)
				C(4)T-C(5)T-T-N(1)T	177.6 (6)
				C(4)T-C(6)T-T-N(2)T	179.1 (11)

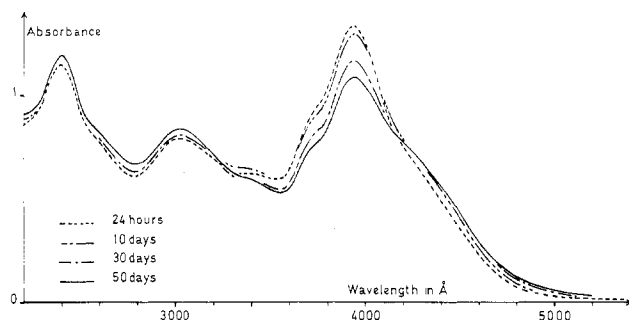


Figure 1. Gradual occurrence of a new band (shoulder at ~ 4300 Å) in the spectrum of a mixture of solutions of $\text{Cu}(\text{salphen})$ (3×10^{-5} M) and TCNQ (1.5×10^{-5} M) in acetonitrile.

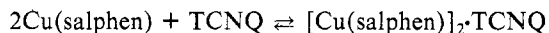
These initial observations were in distinct contrast with the fact that a definite molecular adduct $[\text{Cu}(\text{salphen})]_2 \cdot \text{TCNQ}$ can be isolated under certain conditions of crystallization.

This adduct is largely dissociated in solution as is evidenced by molecular weight determinations which lead to a value of 456 g compared to the calculated molecular weight, 959.97 g, for the $[\text{Cu}(\text{salphen})]_2 \cdot \text{TCNQ}$ formula. On the other hand, the absorption spectra of solutions of the adduct in acetone or acetonitrile show in addition to the spectra of the component molecules a new band (shoulder) at ~ 4300 Å.

As a matter of fact, this new band at ~ 4300 Å, which could not be detected when the measurements were made immediately after mixing or 24 h thereafter, does gradually occur

after a much longer period of time (Figure 1) in the spectra of mixtures of solutions of $\text{Cu}(\text{salphen})$ and TCNQ in acetonitrile.

A possible interpretation of these observations is that an equilibrium of the following type may exist:



where the rate of formation of the adduct may be slow. Therefore rapid evaporation of the reaction mixture induces the precipitation of the component molecules while a very slow evaporation yields the adduct.

If this interpretation is correct, it suggests that one cannot infer that there is no adduct formation simply on the basis of the absorption spectra of the initially mixed component molecules.²⁰

The Crystal Structure. The unit cell contains a pair of centrosymmetrically related $\text{Cu}(\text{salphen})$ molecules and a centrosymmetrical TCNQ molecule. A stereoview is given in Figure 2. The atom-labeling scheme and the anisotropic thermal ellipsoids of the component molecules are illustrated in Figure 3. Bond lengths and angles are summarized in Table III. Some least-squares planes of best fit and the corresponding atom-to-plane distances are presented in Table IV.

The whole $\text{Cu}(\text{salphen})$ molecule (Figure 3a) appears to be nearly planar: the distances of its 25 nonhydrogen component atoms to the least-squares plane range from 0.013 to 0.179 Å with a mean value of 0.077 Å (plane 1 in Table IV). The slight deviation from strict planarity mainly arises from the

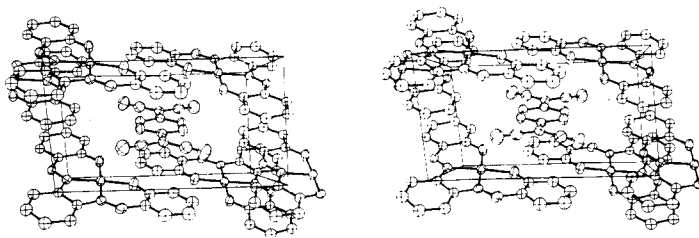


Figure 2. Stereoscopic view of one unit cell, viewed down the b axis. The a axis is horizontal.

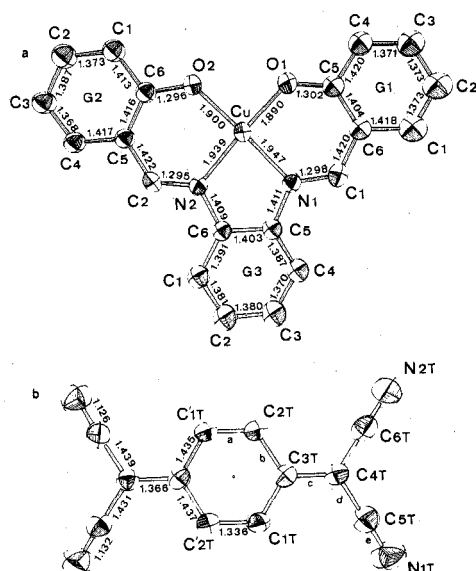


Figure 3. View of the component molecules (Cu(salphen) (a) and TCNQ (b)) showing the atom numbering scheme and the thermal ellipsoids drawn at their 50% probability level.

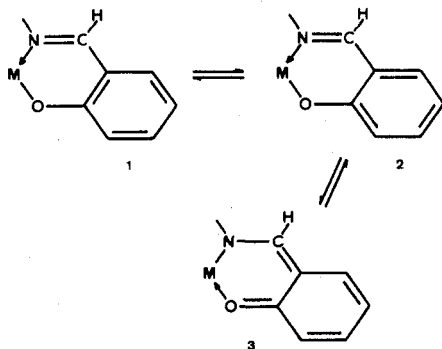


Figure 4. Resonance structures for the molecule of Cu(salphen).

fact that the Cu environment is a little distorted from square planar to tetrahedral, as can be seen from the atom-to-plane distances for Cu, O(1), O(2), N(1), and N(2) atoms (plane 2 in Table IV). The values of the Cu–N bond lengths (1.947 (3) and 1.939 (3) Å) are among the lowest previously reported for copper(II) salicylaldimino derivatives (1.94–1.98 Å),²⁵ those of the Cu–O bond lengths (1.890 (3) and 1.900 (3) Å) are close to the average values previously reported (1.88–1.92 Å). It should be noted, however, that the symmetry around the copper atom in previously reported compounds (distorted square pyramid or distorted tetrahedron) is different from the square-planar configuration found here. The next nearest atom to Cu, apart from those of the directly bonded salicylaldimino group, is located at 3.160 (4) Å under the mean plane of atoms bonded to Cu: this is atom C(4)G2 of the neighboring Cu(salphen) molecule derived from its given position by inversion through the origin and translation +*b*.

The structure of the molecule of Cu(salphen) in the present compound may be discussed in the light of the structural analysis made by Nardin and co-workers²⁶ of both the free ligand, salphen, and the square-planar complex Co^{II}(salphen). From geometrical data, these authors established the free

Table IV. Least-Squares Planes

Atom-to-Plane Distances (Å)						
	plane 1	plane 2	plane 3	plane 5	plane 7	
Cu	-0.0426	-0.0143				
O(1)	-0.1789	-0.0398	0.0102			
O(2)	0.0541	0.0420		-0.0194		
N(1)	-0.0139	0.0510	-0.0036		0.0072	
N(2)	0.0492	-0.0343		0.0180	-0.0077	
C(1)	0.0750		-0.0004			
C(2)	-0.0290			-0.0144		
C(5)G1			-0.0174			
C(6)G1			0.0117			
C(5)G2				-0.0074		
C(6)G2				0.0242		
C(5)G3					-0.0132	
C(6)G3					0.0140	
C(1)G1	0.1705		-0.0014			
C(2)G1	0.1251		0.0024			
C(3)G1	-0.0367		-0.0003			
C(4)G1	-0.1514		-0.0029			
C(5)G1	-0.1002		0.0038			
C(6)G1	0.0573		-0.0017			
C(1)G2	0.1153			plane 6		
C(2)G2	0.0693			0.0035		
C(3)G2	-0.0478			0.0071		
C(4)G2	-0.0945			-0.0082		
C(5)G2	-0.0286			-0.0028		
C(6)G2	0.0471			0.0145		
C(1)G3	0.1328			-0.0139	plane 8	
C(2)G3	0.0684				0.0090	
C(3)G3	-0.0653				0.0101	
C(4)G3	-0.0964				-0.0141	
C(5)G3	-0.0132				-0.0000	
C(6)G3	0.0562				0.0190	
					-0.0232	
C(1)T	plane 9		plane 10		plane 11	
C(2)T	-0.0027		-0.0012		N(1)T	0.0085
C(3)T	0.0087		-0.0011		N(2)T	0.0092
C(4)T	0.0024		0.0036		C(3)T	0.0088
C(5)T	-0.0123		-0.0013		C(4)T	-0.0099
C(6)T	-0.0072				C(5)T	-0.0084
N(1)T	-0.0100				C(6)T	-0.0084
N(2)T	0.0124					
	0.0085					

Coefficients of Planes^a

coeff	plane 1	plane 2	plane 3	plane 4	plane 5	plane 6
A	0.1578	0.2175	0.1404	0.1554	0.1194	0.0916
B	-0.5122	-0.5200	-0.4283	-0.4072	-0.5049	-0.5429
C	0.8443	0.8260	0.8926	0.9000	0.8549	0.8348
D	1.6368	1.5797	1.4954	1.3642	1.5802	1.8471

coeff	plane 7	plane 8	plane 9	plane 10	plane 11
A	0.1823	0.2123	0.0874	0.0829	0.0884
B	-0.5245	-0.5550	-0.3228	-0.3298	-0.3200
C	0.8317	0.8043	0.9424	0.9404	0.9433
D	1.6287	1.6723	-1.9342	-1.8731	-1.9479

Angles between Planes

plane 3–plane 4 = 1.7°; plane 9–plane 10 = 0.6°; plane 1–plane 9 = 12.9°; plane 5–plane 6 = 2.9°; plane 3–plane 11 = 7.5°; plane 7–plane 8 = 2.9°; plane 4–plane 11 = 6.8°

^a The equation of a plane is of the form $AX + BY + CZ + D = 0$ referred to an orthogonal system.

ligand to have an enolimine form in the solid state. Upon coordination, distances such as O(1)–C(5)G1 and C(1)–C(6)G1 shrink by about 0.05 and 0.03 Å, respectively. This led them to suggest for the Co(salphen) molecule a resonance scheme in which the contribution of a ketamine form is as important as that of the enolimine. This scheme is presented in Figure 4: the structures 1 and 2 are predominant in the free ligand while upon coordination the contribution of structure 3 becomes more important. A similar shortening of the distances O(1)–C(5)G1 (1.302 (5) Å), O(2)–C(6)G2 (1.296 (5) Å), C(1)–C(6)G1 (1.420 (6) Å), and C(2)–C(5)G2

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- (26) Pahor, N. B.; Calligaris, M.; Delise, P.; Dodic, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2478.

Table V. Atom-to-Plane Distances (Å) in the Overlapping Parts (See Text)

atom	plane	dist	atom	plane	dist
C(1)T	(O(1), C(5)G1, C(4)G1) ⁱⁱⁱ	3.733 (7)	C(2)	(C(2)G2, C(3)G2, C(4)G2) ⁱⁱⁱ	3.308 (6)
C(3)T	(C(3)G1, C(4)G1, C(5)G1) ⁱⁱ	3.551 (6)	C(3)G2	(N(2), C(2), C(5)G2) ⁱⁱⁱ	3.327 (7)
C(4)T	(C(1)G1, C(2)G1, C(3)G1) ⁱⁱ	3.437 (6)	C(4)G2	(C(5)G2, C(6)G2, C(1)G2) ⁱⁱⁱ	3.394 (5)
C(5)T	(C(1)G1, C(2)G1, C(6)G1) ⁱⁱ	3.442 (6)	C(5)G2	(C(2)G2, C(3)G2, C(4)G2) ⁱⁱⁱ	3.364 (8)
C(4)T	(O(1), C(4)G1, C(5)G1)	3.318 (5)	C(2)G3	(C(1)G3, C(2)G3, C(3)G3) ⁱ	3.38 (1)
C(5)T	(O(1), C(5)G1, C(6)G1)	3.293 (8)	C(3)G3	(C(1)G3, C(2)G3, C(3)G3) ⁱ	3.38 (1)
N(1)T	(O(1), N(1), C(1))	3.355 (5)	C(4)G3	(C(1)G3, C(2)G3, C(3)G3) ⁱ	3.340 (6)
N(1)T	(Cu, C(1), C(5)G1)	3.304 (6)	N(2) ⁱⁱ	(C(2)G2, C(4)G2, C(6)G2) ⁱⁱⁱ	3.289 (4)
C(6)T	(C(3)G1, C(4)G1, C(5)G1)	3.478 (7)	C(2) ⁱⁱ	(O(2), C(1)G2, C(5)G2) ⁱⁱⁱ	3.237 (5)
N(2)T	(C(2)G1, C(3)G1, C(4)G1)	3.620 (7)	C(2)G2 ⁱⁱ	(N(2), C(5)G3, C(6)G3) ⁱⁱⁱ	3.346 (5)
C(5)G1	(C(4)T, C(1)T, C(6)T)	3.296 (7)	C(3)G2 ⁱⁱ	(Cu, N(1), N(2)) ⁱⁱⁱ	3.202 (6)
C(4)G1	(C(3)T, C(4)T, C(5)T)	3.351 (9)	C(4)G2 ⁱⁱ	(Cu, O(2), N(2)) ⁱⁱⁱ	3.135 (4)
C(1)G1 ⁱⁱ	(C(4)T, C(5)T, C(6)T)	3.35 (1)	C(5)G2 ⁱⁱ	(O(2), N(2), C(5)G2) ⁱⁱⁱ	3.237 (6)
C(2)G1 ⁱⁱ	(C(4)T, C(5)T, C(6)T)	3.312 (8)	C(6)G2 ⁱⁱ	(N(2), C(2), C(5)G3) ⁱⁱⁱ	3.15 (1)
C(3)G1 ⁱⁱ	(C(2)T, C(3)T, C(4)T)	3.423 (9)	C(6)G3 ⁱⁱ	(C(1)G2, C(2)G2, C(3)G2) ⁱⁱⁱ	3.371 (5)
C(4)G1 ⁱⁱ	(C(1)T, C(2)T, C(3)T)	3.563 (7)			

^a Roman numeral superscripts refer to the following equivalent positions relative to x, y, z : (i) $\bar{x}, \bar{y}, \bar{z}$; (ii) $x, y, 1 + z$; (iii) $\bar{x}, 1 - y, 1 - z$.

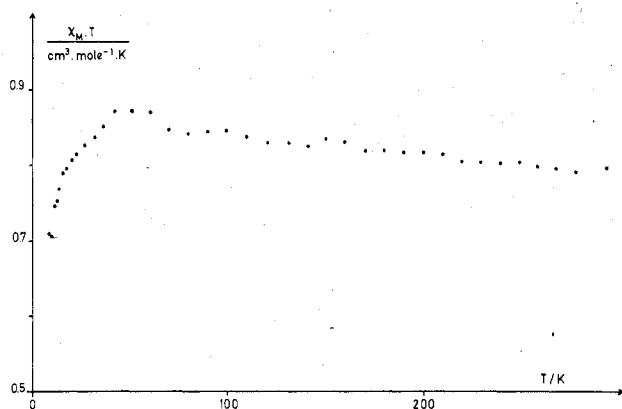


Figure 6. Experimental temperature dependence of the product $\chi_M T$ for [Cu(salphen)]₂·TCNQ.

The magnetic susceptibility of [Cu(salphen)]₂·TCNQ, measured at room temperature, is $2.227 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$. This corresponds to an effective magnetic moment, $\mu_{\text{eff}} = 1.78 \mu_B$, typical of magnetically dilute Cu(II) complexes. The temperature dependence of the magnetic susceptibility is shown in Figure 6. The slight increase of $\chi_M T$ when cooling from 300 to 50 K may be interpreted as resulting from a second-order orbital contribution in the ground-state spin doublet. This is well-known in Cu(II) complexes. The decrease of $\chi_M T$ below 50 K is related to a very small intramolecular coupling within the dimer units or intermolecular coupling, between Cu(II) ions. The ESR spectrum of [Cu(salphen)]₂·TCNQ at 77 K, shown in Figure 7, is a typical axial spectrum with two g values ($g_{\parallel} = 2.180$ and $g_{\perp} = 2.043$) which indicate a $d_{x^2-y^2}$ ground state and a square-planar arrangement about the copper atom in agreement with the crystal structure analysis. The value $\Delta g_{\parallel} / \Delta g_{\perp} = 4.18$ is higher than 4 and indicates that there are no significant exchange interactions.³⁰

Examination of the structure shows that there are neither short Cu–Cu distances nor bridging atoms between copper atoms. The coupling between Cu(II) ions can only arise from π – π interactions either directly between two neighboring stacked molecules of Cu(salphen) or through the molecules of TCNQ. The magnetic susceptibility and ESR results clearly indicate these interactions to be very weak.

The measurements of the powder conductivity of the adduct yielded quite low values ($\sigma \approx 10^{-8} \Omega^{-1} \text{ cm}^{-1}$). However, the conductivities of Cu(salphen) and TCNQ, measured with the

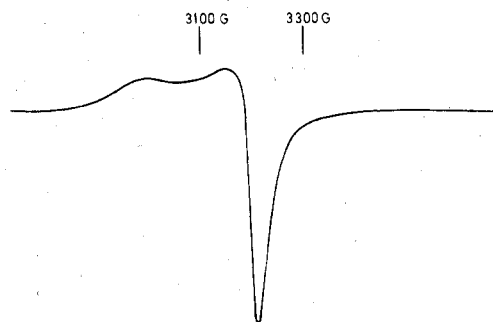


Figure 7. ESR spectrum of solid [Cu(salphen)]₂·TCNQ at 77 K; microwave frequency is 9.133 GHz.

same procedure, are still lower: 10^{-10} and $10^{-9} \Omega^{-1} \text{ cm}^{-1}$, respectively. Moreover, the grinding of the shiny blue-black crystals of [Cu(salphen)]₂·TCNQ, before the preparation of the compressed pellets, resulted in a greenish powder, and this behavior led us to suspect that the structure of the adduct was altered by the grinding. X-ray powder patterns of (i) a finely ground sample (greenish powder) and (ii) an unground microcrystalline sample (blue-black crystals) were taken. Several reflections observed in the second pattern are not present in the first one. It is interesting to note that higher values were obtained for σ , about 10^{-6} to $10^{-7} \Omega^{-1} \text{ cm}^{-1}$, when measuring the conductivity on unground samples with smaller applied force on the pistons of the conductivity press. By increasing this applied force, the structure of the crystals is again altered through the compression process and the conductivity falls to $10^{-8} \Omega^{-1} \text{ cm}^{-1}$. More detailed conductivity studies on single crystals were not possible because of the small size of the crystals.

Multiple phases and polymorphism are very common in charge-transfer complexes. In the case of the complex studied, the extreme sensitivity of its structure to a small change in conditions is further illustrated by the two following experiments: (i) slow evaporation of solutions of the greenish powder obtained after grinding yielded again the blue-black crystals; (ii) slow diffusion of ether into solutions of either the greenish powder or the blue-black crystals yielded brown needles which correspond to a new crystalline species. This high structural variability may be considered as an indication of the weakness of the interactions in the crystals of [Cu(salphen)]₂·TCNQ.

The infrared spectra were obtained in KBr and therefore correspond to that of the greenish powder species. Anyway, as for many weak complexes, there are small differences in frequencies and intensities between the spectra of the adduct and the sum of the contributions from the individual components. However, the two most intense bands of free TCNQ

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(861 and 475 cm^{-1}) are shifted to lower frequencies (830 and 460 cm^{-1}) in the adduct.³¹

Finally the new band observed at $\sim 4300 \text{ \AA}$ in the electronic spectrum of solutions of the adduct may be attributed to what is commonly called an "intermolecular charge transfer" as defined by Mulliken.²⁹ All the points discussed until now indicate that the interaction between TCNQ as an electron acceptor and Cu(salphen) as a donor is extremely weak.

Although no definitive data regarding the orbital interactions are available, the overlap diagram in Figure 5 is instructive in illustrating possible intermolecular interactions. The overlap between TCNQ and Cu(salphen) mainly takes place between the dicyanomethylene groups of TCNQ and the ring O(1)-C(5)G1-C(6)G1-C(1)-N(1) and phenyl group G1 of Cu(salphen). The molecular overlap is not of the ring-to-ring type; this was already noticed concerning the TCNQ-bis(8-hydroxyquinolato)copper(II) complex.¹⁷ One cyano group, C(5)T-N(1)T, lies just over the ring O(1)-C(5)G1-C(6)G1-C(1)-N(1), while the other one, C(6)T-N(2)T, nearly overhangs one side of the phenyl group G1, C(4)G1-C(3)G1. Another phenyl group G1, related to the previous one by translation $+\vec{c}$, covers the ethylenic bond C(3)T-C(4)T, the bond C(4)T-C(5)T, and, partly, the bond C(4)T-C(6)T. From examination of the atom-to-plane distances given in Table V, distances of respectively 3.29 and 3.35 $\text{\AA}$ are observed from atoms C(5)T and N(1)T to the ring O(1)-C(5)G1-C(6)G1-C(1)-N(1). With the idea that the electronic density of Cu(salphen) is most likely delocalized over the whole molecule, these relatively short distances could be indicative

of interaction between both molecules. The distances to the plane of the cyanomethylene group of the overlying atoms (C(1)G1 and C(2)G1 (3.35 and 3.31 $\text{\AA}$) and of the underlying atoms C(5)G1 and C(4)G1 (3.30 and 3.35 $\text{\AA}$) are also compatible with intermolecular interactions. The presumed interactions take place at both ends of the molecule of TCNQ linking the component molecules into infinite chains. This arrangement is compatible with the low but nonnegligible electrical conductivity that has been observed.

In conclusion, $[\text{Cu}(\text{salphen})]_2\text{TCNQ}$ is a weak molecular adduct. There are, however, some hints that the charge transfer between the component molecules may not be totally negligible.

Acknowledgment. This work has been technically supported in part by the French CNRS, the DGRST, and the DESR. We thank Dr. R. Haran for recording the ESR spectra, Professor O. Kahn for the magnetic measurements and Dr. L. Interrante and Dr. J. Kasper for helpful comments on the manuscript. The helpful assistance of M. F. Bruniquel is also acknowledged.

Note Added in Proof. Since submission of this paper, the synthesis and structure of a 1:2 molecular complex of bis(*N*-isopropyl-2-oxy-1-naphthylidenaminato)copper(II) with TCNQ has been reported (Matsumoto, N.; Nonaka, Y.; Kida, S.; Kawano, S.; Ueda, I. *Inorg. Chim. Acta* 1979, 37, 27.). The crystal structure of this complex shows what these authors call "a typical II-II type molecular complex structure of alternately stacked donor and acceptor molecules."

Registry No. $[\text{Cu}(\text{salphen})]_2\text{TCNQ}$, 72121-31-4; Cu(salphen), 42490-12-0.

Supplementary Material Available: Listings of structure factor amplitudes and root-mean-square amplitudes of vibration (5 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Uranium(IV) Tetraiodide by X-ray and Neutron Diffraction

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Received July 12, 1979

The crystal structure of uranium tetraiodide has been solved by a combination of X-ray and neutron diffraction techniques. UI_4 is monoclinic, of space group $C2/c$, with $a = 13.967$ (6) $\text{\AA}$, $b = 8.472$ (4) $\text{\AA}$, $c = 7.510$ (3) $\text{\AA}$, and $\beta = 90.54$ (5)°. The uranium atom is at position 4(e) with $y = 0.152$ (2), and the iodine atoms are in general positions 8(f). There are two types of iodine atoms with I(1) at (0.123 (1), 0.118 (2), -0.086 (2)) and I(2) at (-0.134 (1), 0.382 (3), and 0.100 (2)). The structure, based on hexagonal close packing of the iodine atoms, consists of zigzag chains $\text{UI}_2\text{I}_{4/2}$, with the terminal iodine atoms in cis positions. The U-I(1) (bridging) distances are 3.08 (2) and 3.11 (2) $\text{\AA}$, and the U-I(2) (terminal) distances are both 2.92 (2) $\text{\AA}$. The parameters were determined by the neutron powder profile refinement technique, and $R = \sum(|y_o - y_c|)/\sum y_o = 0.13$, $R(\text{expected}) = ((\text{NO} - \text{NV})/\sum w y_o^2)^{1/2} = 0.11$, and $\chi^2 = \sum w(y_o - y_c)^2/(\text{NO} - \text{NV}) = 1.7$. UI_4 is not isostructural with any other known MX_4 halide and is the only actinide tetrahalide to have a chain structure, although chains are common in the transition-metal tetrahalide structures.

Introduction

The existence of uranium tetraiodide has been known for many years, but it has remained structurally uncharacterized because single crystals and good X-ray photographs are very difficult to obtain, and UI_4 is not isostructural with ThI_4 ,¹ UBr_4 ,² or any other known actinide or transition-metal tetrahalide. The present work was undertaken to fill this gap in the MX_4 structure types.

Experimental Section

Approximately 25 g of UI_4 was prepared by reacting uranium metal turnings with iodine, according to the method of Bagnall et al.³ In the final phases of this preparation, excess iodine was sublimed from the UI_4 within the evacuated vessel. The dissociation $\text{UI}_4 \rightarrow \text{UI}_3 + \frac{1}{2}\text{I}_2$ occurs to some extent depending on temperature conditions, generally resulting in a small amount of UI_3 contamination. The moisture-sensitive UI_4 was always handled by drybox methods.

Some needles of UI_4 were mounted with Kel-F grease in glass capillaries. The crystals appeared lathlike under the microscope, with

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