Table I. Details of the Experiment

	Camera distance, cm	T_{sample}, °C	T_{nozzle}, °C	P_{camera}, Torr	Exposure, s	Wavelength, Å	s range, Å^{-1}
F_5SOSF_5	50	−48	10	5×10^{-6}	15–40	0.049 26 (2)	1.4–16.8
	25	−45	10	1×10^{-5}	45–70	0.049 33 (1)	7.0–34.0
$F_5SeOSeF_5$	50	−27	10	2×10^{-6}	45–80	0.049 24 (1)	1.4–17.0
	25	−30	10	5×10^{-6}	120–180	0.049 30 (1)	7.0–34.0
$F_5TeOTeF_5$	50	−36	15	1×10^{-5}	40–70	0.049 31 (1)	1.4–15.0
	25	−32	15	1×10^{-5}	90–180	0.049 32 (1)	8.0–30.0

Table II. Force Constants for Y_2O Skeleton (mdyn Å^{-1}, mdyn, and mdyn Å)

	$Y = SF_5$	$Y = SeF_5$	$Y = TeF_5$
f_r	5.3	4.3	4.4
f_α	2.3	1.5	1.1
f_{rr} [a]	0.8	0.8	0.4
$f_{r\alpha}$ [a]	0.1	0.1	0.1

[a] Assumed.

7 g. The purity of these products was monitored by ^{19}F NMR spectroscopy and was always found better than 99%. The diffraction intensities were recorded with a Balzers diffractograph KDG 2[12] for two camera distances (50 and 25 cm). The accelerating voltage was approximately 60 kV and the wavelength was determined from ZnO diffraction patterns. Details of the experiment are summarized in Table I. Kodak electron image plates were used for the sulfur derivative and Ilford N50 plates for the selenium and tellurium compounds. Three plates of each data set were reduced by the usual procedure[13] of this laboratory. For the short camera distance, intensities recorded without gas were subtracted. The background was refined separately for each recording. The averaged molecular intensities $sM(s)^{\text{exptl}}$ for the two camera distances are presented in Figures 2, 4, and 6.

Vibrational Analysis

The infrared and Raman spectra[9,10] show many low vibrational frequencies for these molecules. Thus, rather large perpendicular mean-square amplitudes are expected which may have a considerable effect on the geometric parameters determined by electron diffraction. To account for these effects, the shrinkage corrections $\Delta r = r_a - r_\alpha{}^0$[14] were estimated from a very crude force field. For the XF_5 groups the force constants of the respective XF_6[15] molecules were transferred. The force constants characterizing the vibrations of the Y_2O molecular skeleton ($Y = XF_5$) were calculated with a three-mass-model from the frequencies $\nu_s(Y_2O)$, $\nu_a(Y_2O)$, and $\delta(Y_2O)$.[10] The bending vibration for the sulfur compound which is not given in ref 10 was assigned to a very strong raman band at 265 cm^{-1}. The force constants for the Y_2O skeleton are listed in Table II. . From the vibrational spectra no information about the torsion of the XF_5 groups around the O–X bond can be obtained. As was demonstrated in the case of perfluoroneopentane,[16] the torsional motions have a strong effect on the mean-square amplitudes of some nonbonded distances and on the skrinkage corrections for distances which are independent of torsion. For these distances the torsional contributions were neglected. For all three compounds a torsional force constant $f\tau = 0.5$ mdyn Å was used in the spectroscopic calculations. This value is based on two considerations: (1) the X–O bond distances indicate a considerable double bond character and (2) the effective deviation of the XF_5 groups from the eclipsed position is <4° (see Structure Analysis). The shrinkage corrections calculated with these crude force fields are listed in Table III. The corrections for the Y_2O skeleton are smaller than expected from the vibrational spectra.

Structure Analysis

Preliminary geometric parameters and the orientation of the XF_5 groups around the O–X bond were determined by analyzing the radial distribution functions (Figures 3, 5, and 7). Comparing theoretical radial distribution functions for various models with the experimental function demonstrates that approximate agreement between model and experiment is obtained with a C_{2v} model and dihedral angles $\delta(XOXF_{eq}) \sim 45°$; i.e., the equatorial fluorine atoms are eclipsed. These preliminary models were refined in a least-squares analysis, based on the molecular intensities. The diagonal elements of the weight matrix increased exponentially for $1.4 < s < 4$ Å^{-1} and decreased exponentially for $14 < s < s_{\max}$ for the 50-cm data. For the short camera distance the respective ranges were $s_{\min} < s < 9$ Å^{-1} and $30 < s < 34$ Å^{-1}. For the 25-cm data of the tellurium compound the weight decreased for $25 < s < 30$ Å^{-1}. For both camera distances an s interval of $\Delta s = 0.2$ Å^{-1} was chosen. Scattering amplitudes and phases published by Haase[17] were used in the calculations. For $F_5Te–O–TeF_5$ we also calculated a least-squares refinement with the scattering amplitudes and phases of Schäfer et al.[18] The differences in the geometric parameters were negligible (~0.001 Å for bond distances) and for the mean-square amplitudes the differences were smaller than the error limits. The $r_a - r_\alpha{}^0$ corrections were included in the least-squares procedure. Assuming C_{4v} symmetry for the XF_5 groups, various possible distortions of the $-XF_5$ group were considered: (1) deviation of the angle $F_{ax}XF_{eq}$ from 90°, (2) tilt of the XF_5 group with respect to the O–X bond direction, (3) deviation of the dihedral angle $\delta(XOXF_{eq})$ from 45°. In the last case the XF_5 groups were rotated in opposite directions; i.e., the overall symmetry of the molecule was C_2. Since the distortions (2) and (3) were smaller than the respective error limits for all three molecules, they were not considered in the further calculations. Assuming $(X–F)_{eq} = (X–F)_{ax}$ an average value $(X–F)_{av}$ for this bond length was obtained from a least-squares analysis. Refining the X–F distances separately resulted in high correlations and large standard deviations for these parameters and thus did not lead to any conclusive result because of the large error limits. For the sulfur compound $r_{ax} > r_{eq}$ while for the selenium and tellurium compounds $r_{ax} < r_{eq}$. In all cases, however, the differences between r_{ax} and r_{eq} are smaller than the error limits. The average X–F dis-

Table III. Corrections $\Delta r = r_a - r_\alpha{}^0$ for $(XF_5)_2O$ in Angstrom Units

	F_5SOSF_5	$F_5SeOSeF_5$	$F_5TeOTeF_5$
X–O	0.001	0.001	0.002
X–F	0.002	0.004	0.006
$O\cdot\cdot F_{ax}$	0.002	0.003	0.005
$O\cdot\cdot F_{eq}$	0.000	0.001	0.002
$F_{ax}\cdot\cdot F_{eq}$	0.001	0.001	0.002
$F_2\cdot\cdot F_3$	0.001	0.001	0.003
$F_2\cdot\cdot F_4$	0.000	0.001	0.001
$X\cdot\cdot X'$	0.000	0.000	0.000
$X\cdot\cdot F_1''$	0.001	0.001	0.002
$X\cdot\cdot F_2'$	0.000	0.000	0.000
$X\cdot\cdot F_3'$	0.000	0.000	−0.001
$F_1\cdot\cdot F_1'$	0.001	0.001	0.002
$F_1\cdot\cdot F_2'$	0.000	0.000	0.001
$F_1\cdot\cdot F_3'$	0.001	0.000	0.000
$F_2\cdot\cdot F_2'$	0.000	0.000	−0.001
$F_2\cdot\cdot F_3'$	0.001	0.000	0.000
$F_2\cdot\cdot F_4'$	−0.003	−0.004	−0.004
$F_2\cdot\cdot F_4'$	0.003	0.003	0.003
$F_3\cdot\cdot F_3'$	0.001	0.001	0.000
$F_3\cdot\cdot F_5'$	−0.004	−0.006	−0.007

(27) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 71.
(28) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(29) Reference 27, p 149.
(30) C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "ALFF, Ames Laboratory Fast Fourier", Iowa State University, 1971.
(31) P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, American Crystallographic Association Program Library (old) No. 317, modified.
(32) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(33) T. J. Kistenmacher, L. G. Marzilli, and D. J. Szalda, *Acta Crystallogr., Sect. B*, **32**, 186 (1976).
(34) T. J. Kistenmacher and D. J. Szalda, *Acta Crystallogr., Sect. B*, **31**, 1659 (1975).
(35) T. J. Kistenmacher, D. J. Szalda, and L. G. Marzilli, *Acta Crystallogr., Sect. B*, **31**, 2416 (1975).
(36) J. D. Bell, H. C. Freeman, A. M. Wood, R. Driver, and W. R. Walker, *Chem. Commun.*, 1441 (1969).
(37) E. I. Solomon, J. W. Hare, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 1389 (1976).
(38) J. S. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1349 (1975).
(39) G. V. Chapman, P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *J. Mol. Biol.*, **110**, 187 (1977).
(40) P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, M. P. Venkatappa, and L. E. Vickery, *J. Mol. Biol.*, **112**, 649 (1977).
(41) Y. N. Chirgadze, M. B. Garber, and S. V. Nikonov, *J. Mol. Biol.*, **113**, 443 (1977).
(42) E. T. Adman, R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, American Crystallographic Association Summer Meeting, Michigan State University, Aug 7–12, 1977.

Contribution from the Institut für Physikalische und Theoretische Chemie der Universität, 7400 Tübingen, West Germany, and the Anorganisch Chemisches Institut der Universität, 6900 Heidelberg, West Germany

Electron Diffraction Study of Bis(pentafluorosulfur), Bis(pentafluoroselenium), and Bis(pentafluorotellurium) Oxides[1]

HEINZ OBERHAMMER* and KONRAD SEPPELT

Received November 15, 1977

High purity F_2S–O–SF_5, F_5Se–O–SeF_5, and F_5Te–O–TeF_5 have been prepared and structurally investigated by electron diffraction. All three molecules have the structure of two linked octahedra with an oxygen bridge. The bridge angle is surprisingly high and constant (about 143°) in all three molecules, although steric hindrance diminishes considerably in the sequence F_5S–O–SF_5 > F_5Se–O–SeF_5 > F_5Te–O–TeF_5. The equatorial fluorine atoms have an eclipsed orientation. This effect and the high bridging angle may best be described in terms of some $(pd)_\pi$ bonding.

Introduction

F_5SOSF_5, $F_5SeOSeF_5$, and $F_5TeOTeF_5$ are chemically strongly related to the hexafluorides SF_6, SeF_6, and TeF_6. A large amount of work, both experimental and theoretical, has been done for the bonding problem in the hexafluorides,[2] although a final answer on the question of d-orbital participation in the bonding cannot be given. We choose the title molecules, as their more complicated structure could give an answer on this important question, whereas in the simple hexafluorides the octahedral configuration is not affected by the bonding type.

All three compounds are known; F_5Se–O–SeF_5 was the last one to be prepared,[3,4] as synthetical problems with six-valent selenium are often larger than with S(VI) and Te(VI). The compounds are best prepared according the following equations:

$$2SF_4 + OF_2 \xrightarrow{-78\ ^\circ C,\ h\nu} F_5S\text{–O–}SF_5$$

$$Xe(OSeF_5)_2 \xrightarrow{130\ ^\circ C} Xe + {}^1/{}_2O_2 + F_5Se\text{–O–}SeF_5{}^3$$

$$TeO_2 \xrightarrow{F_2/N_2} F_5Te\text{–O–}TeF_5{}^5$$

Their ^{19}F NMR spectra gave evidence for the structure of the compounds. The ab_4 spectra prove the square-pyramidal orientation of the $-SF_5$, $-SeF_5$, and $-TeF_5$ groups. Some long range coupling in terms of $aa'b_4b_4'$ spectra were observed as well.[6-8]

The vibrational spectroscopy led to an estimation of a bridge angle of 130° in F_5Te–O–TeF_5,[9,10] that is not too far from the correct value of 145.5° if one considers the gross assumptions made. Of course, no information was known about the torsional orientation of the two bulky groups. A brief communication of the results has been published recently.[11]

Experimental Section

Materials. Bis(pentafluorosulfur) Oxide. A mixture of 54 g of sulfur tetrafluoride (Air Products, technical grade) and 13 g of oxygen difluoride (Matheson Co., technical grade) is condensed into a Pyrex glass tube that is then sealed off. *Caution*! This mixture is a possible explosive! At −110 °C the mixture is shaken in order to achieve a homogenous solution. At −78 °C the liquid is irradiated through the walls of an unsilvered glass Dewar by a 500-W focusable high-pressure mercury lamp. After 3 days of irradiation, when the yellow-brown color of OF_2 has disappeared, the glass is opened at −197 °C. The product consists of O_2, OF_2, SF_6, SO_2F_2, SOF_4, SOF_2, SF_4, F_5SOSF_5, F_5SOOSF_5, $F_5SOSF_4OSF_5$ and higher boiling liquids. Conventional trap to trap distillation at −120 °C removes O_2, OF_2, and part of SF_6 as well as the high boiling materials. The remainder is hydrolyzed in a 200-mL stainless steel container by 80 mL of concentrated KOH/H_2O solution. The volatile materials (SF_6, F_5SOSF_5, and F_5SOOSF_5 besides some water) are heated in a stainless steel container to 250 °C in order to destroy the peroxides. The resulting mixture is again hydrolyzed as described above, dried by P_2O_5 and statically distilled on a glass vacuum line to remove the last traces of SF_6 and F_5S–O–SF_4. F_5SOSF_5 is a colorless liquid (bp 31.5 mp −118 °C) extremely stable toward hydrolysis and heat, yield 12.5 g.

Bis(pentafluoroselenium) Oxide. Cf. ref 3. $Xe(OSeF_5)_2$ (30 g), prepared as described elsewhere,[2] is pyrolyzed in a 100-mL stainless steel container at 150 °C for 2 h. Products are O_2, Xe, SeF_6, $F_5SeOSeF_5$, SeF_4, and $SeOF_2$. Alkaline hydrolysis (as described above) removes SeF_4 and $SeOF_2$. After drying with P_2O_5, static trap to trap distillation removes the other impurities. F_5Se–O–SeF_5 (bp 53 °C, mp −85 °C) is a colorless liquid, very much like its sulfur analogue, yield 3.5 g.

Bis(pentafluorotellurium) Oxide. Cf. ref 5. TeO_2 (100 g) is fluorinated in a copper vessel by a stream of F_2/N_2 1:10 at 60 °C. All volatile materials except fluorine are trapped by a liquid oxygen trap. The main product TeF_6 is carefully removed by static trap to trap distillation at −100 °C. The liquid residue is heated to 180 °C in a stainless steel cylinder to destroy $F_5TeOOTeF_5$, the resulting mixture is washed with 50% sulfuric acid, dried over P_2O_5, and purified by trap to trap distillation. F_5Te–O–TeF_5 is a colorless liquid (bp 59.8 °C, mp −36.6 °C) not stable toward alkaline hydrolysis, yield

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* To whom correspondence should be addressed at Universität Tübingen.

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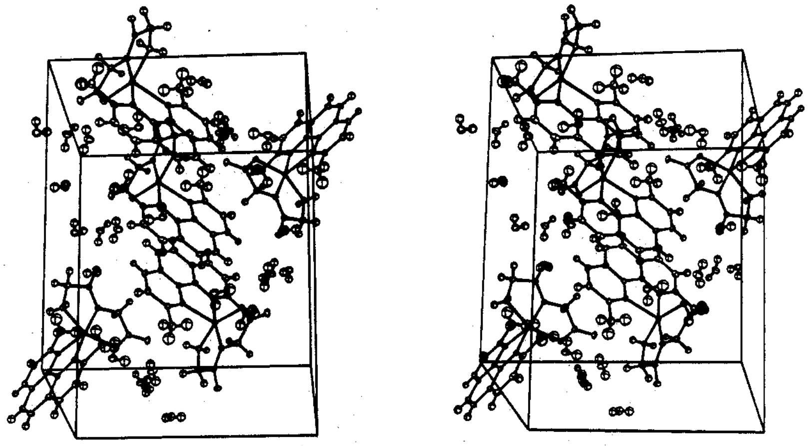

Figure 3. Stereoview of the crystal structure of (2,9-dimethyl-1,10-phenanthroline)(glycylglycinato)copper(II) pentahydrate, showing ellipsoids of 15% probability.[32] The view is approximately into the positive *a* direction, with *b* horizontal and *c* vertical in the plane of the page.

Table V. Deviations of Atoms from the Planes of the Four Closest Ligand Atoms

Complex	Deviations of ligand atoms from the plane,[a] Å				
Cu(gg)·3H_2O[b]	NH_2	N	O^-	H_2O	Cu
	+0.125	−0.148	+0.137	−0.114	+0.156
	NH_2	N	O^-	H_2O	Cu
	+0.029	−0.033	+0.030	−0.026	+0.244
Cu(gg)·2H_2O[c,d]	NH_2	N	O^-	H_2O	Cu
	+0.013	−0.015	+0.014	−0.011	+0.170
Cu(gg)(H_2O)-(9-methyl-adenine)·4H_2O[e]	NH_2	N	O^-	Adenine N	Cu
	+0.121	−0.145	+0.130	−0.106	+0.190
Cu(gg)(phen)·3H_2O[d,f]	NH_2	N	O^-	phen N	Cu
	−0.056	+0.067	−0.060	+0.049	+0.146
Cu(gg)(dmp)·5H_2O[g]	NH_2	N	O^-	dmp N	Cu
	−0.139	+0.130	−0.079	+0.089	+0.254

[a] These are four-atom planes. Cu was excluded from the calculation. [b] Reference 4. [c] Reference 34. [d] This least-squares plane was calculated from the information given in the references cited. [e] Reference 33. [f] Reference 7. [g] This work.

cussion because the manner of glycylclycinato coordination in Cu(gg)(dmp) is qualitatively different.

Three water molecules hydrogen bond to Cu(gg)(dmp), and two others per asymmetric unit hydrogen bond to each other and to the first three as shown in Figure 3. The hydrogen bond lengths and angles are given in Table III. Note that all of the O—H···O angles are near 180°, as appropriate.

Conclusion

The molecular structure of Cu(gg)(dmp)·5H_2O is considerably distorted from square-pyramidal geometry, as expected. The extinction coefficient of the complex at its visible band of maximum absorption is 313, more than three times larger than those of comparable Cu(II) complexes with small peptides.[7] The Cu(II) ion is 0.254 Å out of the basal plane in this complex in the direction of the axial ring nitrogen atom, and the complex is unstable in solution.

The accumulated information on the crystal structures of Cu(II) complexes with small peptides clearly shows that a somewhat distorted square-pyramidal geometry is preferred.[4–7] The EPR parameters of this complex are similar to those of synthetic copper peptides (including that with insulin), and not to those of the "blue" copper proteins, for which a flattened tetrahedral environment is expected around copper.[37] A distorted square plane, with or without axial ligands, is likely to be important in copper proteins classified as "nonblue" as well as in synthetic copper peptides. There is, to date, one reported crystal structure of a copper protein;[38] the environment of copper in the copper–zinc protein bovine superoxide dismutase is distorted square planar with four imidazole rings as the ligands to copper.[38] On-going investigations of the crystal structures of some of the "blue" copper proteins are still in preliminary stages.[39–42]

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM18813-06). We are also indebted to the University of Hawaii Computing Center, and to Daniel Chan of the Department of Biochemistry and Biophysics of the University of Hawaii School of Medicine for performing the EPR measurements.

Registry No. Cu(gg)(dmp)·5H_2O, 65890-22-4.

Supplementary Material Available: Listing of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) S. N. Choi, R. D. Bereman, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 2087 (1975).
(2) L. S. Childers, K. Folting, L. L. Merritt, Jr., and W. E. Streib, *Acta Crystallogr., Sect. B*, **31**, 924 (1975).
(3) R. D. Bereman, F. T. Wang, J. Najdzionek, and D. M. Braitsch, *J. Am. Chem. Soc.*, **98**, 7266 (1976).
(4) H. C. Freeman in "The Biochemistry of Copper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, pp 77–113.
(5) H. C. Freeman, *Adv. Protein Chem.*, **22**, 257–424 (1967).
(6) H. C. Freeman in "Inorganic Biochemistry", G. L. Eichhorn, Ed., Vol. 1, Elsevier, Amsterdam, 1973, pp 121–166.
(7) M. C. Lim, E. Sinn, and R. B. Martin, *Inorg. Chem.*, **15**, 807 (1976).
(8) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(9) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, Oxford, 1965, pp 65–66.
(10) R. S. Giordano and R. D. Bereman, *J. Am. Chem. Soc.*, **96**, 1019 (1974).
(11) P. W. Selwood, "Magnetochemistry", Interscience, New York, N.Y., 1956, p 78.
(12) J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, **16**, 34 (1963).
(13) J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, **15**, 480 (1962).
(14) B. Strandberg, I. Lindqvist, and R. Rosenstein, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **116**, 266 (1961).
(15) M. K. Kim and A. E. Martell, *Biochemistry*, **3**, 1169 (1964).
(16) W. L. Koltun, M. Fried, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **82**, 233 (1960).
(17) J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.*, **19**, 253 (1976).
(18) B. J. Hathaway and P. G. Hodgson, *J. Inorg. Nucl. Chem.*, **35**, 4071 (1973).
(19) R. D. Bereman and D. J. Kosman, *J. Am. Chem. Soc.*, **99**, 7322 (1977).
(20) J. F. Boas, J. R. Pilbrow, C. R. Hartzell, and T. D. Smith, *J. Chem. Soc., A*, 572 (1969).
(21) G. F. Bryce, *J. Chem. Phys.*, **70**, 3549 (1966).
(22) H. Yokoi, M. Sai, T. Isobe, and S. Ohsawa, *Bull. Chem. Soc. Jpn.*, **45**, 2189 (1972).
(23) R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).
(24) T. Ottersen, LP-76 Computer Program, University of Hawaii, 1976.
(25) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).
(26) T. Ottersen, ABSCO computer program, Chemistry Department, University of Oslo, 1974.

Table III (*Continued*)

C(10)-C(9)-H(9)	118 (2)	H(14A)-C(14)-H(14C)	112 (4)
C(10)-C(11)-H(11)	119 (2)	H(14A)-C(14)-H(14B)	105 (4)
H(11)-C(11)-C(12)	121 (2)	H(14B)-C(14)-H(14C)	104 (4)
C(11)-C(12)-H(12)	122 (2)	H(21A)-C(21)-H(21B)	114 (2)
H(12)-C(12)-C(13)	118 (2)	H(25A)-C(25)-H(25B)	110 (2)
C(13)-C(14)-H(14A)	109 (3)	H(26A)-N(26)-H(26B)	113 (3)
C(13)-C(14)-H(14B)	111 (3)	H(27A)-O(27)-H(27B)	110 (5)
C(13)-C(14)-H(14C)	116 (3)	H(28A)-O(28)-H(28B)	102 (5)
		H(29A)-O(29)-H(29B)	108 (4)
		H(30A)-O(30)-H(30B)	98 (5)
		H(31A)-O(31)-H(31B)	109 (4)
C. Selected Torsion Angles, Deg			
N(22)-C(23)-C(25)-N(26)	9.5	O(18)-C(19)-C(21)-N(22)	9.6
C(21)-N(22)-C(23)-C(25)	177.2	N(2)-C(17)-C(16)-N(15)	1.3
C(19)-C(21)-N(22)-C(23)	158.7	C(7)-C(17)-C(16)-C(10)	0.8

[a] The esd is in the units of the least significant digit given for the corresponding parameter.

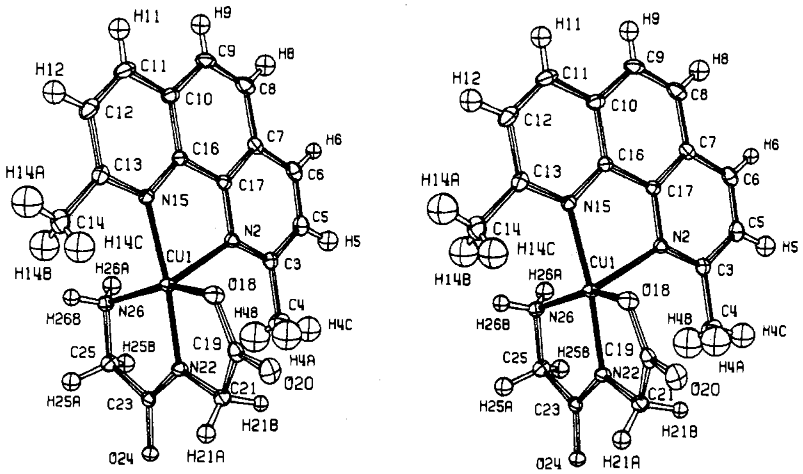

Figure 2. Stereoview of the (2,9-dimethyl-1,10-phenanthroline)(glycylglycinato)copper(II) complex showing ellipsoids of 50% probability.[32]

Table IV

Coefficients of Least-Squares Planes $Ax + By + Cz = D$

Plane	Atoms in plane	*A*	*B*	*C*	*D*	Distance from plane, Å
I	Cu(1), O(18), C(19), C(21), N(22)	−0.8125	0.5806	0.0521	−0.8703	Cu(1), −0.001; O(18), 0.045; C(19), −0.012; C(21), −0.122; N(22), −0.001
II	Cu(1), N(22), C(23), C(25), N(26)	0.6259	−0.7753	0.0843	0.5846	Cu(1), 0.001; N(22), −0.011; C(23), −0.017; C(25), 0.084; N(26), −0.057
III	Cu(1), O(18), C(19), C(21), N(22), C(23), C(25), N(26)	0.7592	−0.6349	0.1436	1.3004	Cu(1), 0.015; O(18), −0.254; C(19), −0.051; C(21), 0.370; N(22), 0.229; C(23), 0.119; C(25), −0.087; N(26), −0.341
IV	Cu(1), N(2), N(15), C(16), C(17)	−0.7074	−0.6439	0.2915	−1.6947	Cu(1), 0.000; N(2), −0.004; N(15), 0.000; C(16), −0.004; C(17), 0.008
V	Cu(1), N(2), N(15), C(3)-C(14), C(16), C(17)	−0.7112	−0.6441	0.2816	−1.7374	Cu(1), 0.001; N(2), −0.003; C(3), −0.017; C(4), −0.072; C(5), −0.005; C(6), 0.013; C(7), 0.027; C(8), 0.029; C(9), 0.013; C(10), 0.005; C(11), −0.043; C(12), −0.045; C(13), −0.001; C(14), 0.029; N(15), 0.022; C(16), 0.022; C(17), 0.024
VI	C(10), C(11), C(12), C(13), N(15), C(16)	−0.7259	−0.6364	0.2610	−1.7606	C(10), 0.009; C(11), −0.006; C(12), −0.006; C(13), 0.008; N(15), −0.002; C(16), −0.004
VII	N(2), C(3), C(5), C(6), C(7), C(17)	−0.7061	−0.6426	0.2974	−1.6769	N(2), −0.001; C(3), −0.001; C(5), 0.003; C(6), −0.001; C(7), −0.003; C(17), 0.003
VIII	C(7), C(8), C(9), C(10), C(16), C(17)	−0.7157	−0.6410	0.2774	−1.7342	C(7), −0.002; C(8), 0.006; C(9), −0.001; C(10), −0.005; C(16), 0.005; C(17), −0.003
IX	N(15), O(18), N(22), N(26)	−0.7250	0.6884	0.0227	−0.3421	Cu(1),[a] −0.254, N(15), −0.089; O(18), 0.079; N(22), −0.130; N(26), 0.139

Interplanar Angles, Deg

I–II	III–V	VI–VII	VI–VIII	VII–VIII
17.4	95.2	2.4	1.1	1.3

[a] This atom was not included in the calculation of the least-squares plane.

ole)·1.5H_2O (2.04 Å).[36] Also, the copper(II)–carboxylate oxygen bond (2.033 Å) is somewhat longer than that reported for Cu(gg)·3H_2O (1.98 Å), Cu(gg)(H_2O)(9-methyladenine)·4H_2O (1.963 Å), Cu(gg)(phen)·3H_2O (2.008 Å), Cu(gg)·2H_2O (1.974 Å), Cu(gg)(cytosine) (1.983 Å), and Cu(gg)(H_2O)(imidazole)·1.5H_2O (2.01 Å). The amide nitrogen–copper distance of 1.900 (2) Å in this structure is similar to those found in the aforementioned complexes.

The crystal structures of glycylglycylglycinato and glycylglycylglycylglycinato complexes of Cu(II) have been reported and have been further discussed in review articles.[4-6] These complexes have not been included in the present dis-

Table VI. X-F Distances (Å) in $F_5X{-}O{-}XF_5$ and XF_6 (r_g values)

X	$F_5X{-}O{-}XF_5$	XF_6	Ref
S	1.563 (4)	1.56 (2)	34
		1.58 (3)	35
		1.565 (10)	36
Se	1.686 (3)	1.67 (3)	34
		1.70 (3)	35
		1.689 (10)	36
Te	1.823 (4)	1.82 (4)	34
		1.84 (3)	35
		1.824 (4)	37
		1.815 (4)	38

$F_5TeOTeF_5$ (r_g(Te–O) = 1.835 (12) Å) is identical with double-bond value in TeO_2[31] (r_g(Te=O) = 1.83 (2) Å).

The partial double-bond character of the X–O bonds is established not only by the short bonds and large angles but by the overall configuration as well, which is eclipsed. Although this eclipsed configuration is sterically highly unfavorable especially in the case of $F_5S{-}O{-}SF_5$, it is nevertheless retained in all three molecules. Instead of $(pd)_\pi$ interaction the double-bond character is sometimes explained in terms of hyperconjugation; the anions SOF_5^-,[32] $SeOF_5^-$,[10] and $TeOF_5^-$[33] are good examples

$$^{-}O{-}SeF_5 \leftrightarrow O{=}SeF_4F^{-} \leftrightarrow \text{etc.}$$

This resonance gives a shortening of the oxygen bond together with a lengthening of the fluoride bonds, especially the axial ones.

We do not think that this explanation may hold for the molecules $F_5X{-}O{-}XF_5$, as there is no indication that the fluorine bonds are lengthened in comparison with the corresponding hexafluorides; see Table VI. Thus some $(pd)_\pi$ bonding is favored as a satisfying explanation for the overall structural behavior of these molecules. Due to the only subtle differences in all three molecules, it might be unreasonable to say which one has the largest $(pd)_\pi$ bonds. $F_5TeOTeF_5$ would be the candidate for it: highest angle in spite of least sterical hindrance and highest X–O bond strength.

Registry No. F_5SOSF_5, 12299-68-2; $F_5SeOSeF_5$, 27218-15-1; $F_5TeOTeF_5$, 20533-01-1; SF_4, 7783-60-0; OF_2, 7783-41-7.

References and Notes

(1) This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.
(2) N. Rösch, V. H. Smith, and M. H. Wangbo, *J. Am. Chem. Soc.*, **96**, 5984 (1974).
(3) K. Seppelt, *Chem. Ber.*, **106**, 157 (1973).
(4) W. L. Reichert and G. H. Cady, *Inorg. Chem.*, **12**, 749 (1973).
(5) Campbell and P. L. Robinson, *J. Chem. Soc.*, 3454 (1956).
(6) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).
(7) K. Seppelt, *Z. Anorg. Allg. Chem.*, **399**, 65 (1973).
(8) P. Bladon, D. H. Brown, K. D. Crosbie, and D. W. A. Sharp, *Spectrochim. Acta*, **261**, 2221 (1970).
(9) H. Bürger, *Z. Anorg. Allg. Chem.*, **360**, 97 (1968).
(10) K. Seppelt, *Z. Anorg. Allg. Chem.*, **399**, 87 (1973).
(11) H. Oberhammer and K. Seppelt, *Angew. Chem., Int. Ed. Engl.*, **17**, 69 (1978).
(12) W. Zeil, J. Haase, and L. Wegmann, *Z. Instrumentenkd.*, **74**, 84 (1966).
(13) H. Oberhammer and J. Strähle, *Z. Naturforsch. A*, **30**, 296 (1975).
(14) K. Kuchitsu and S. J. Cyvin in "Molecular Structures and Vibrations", S. J. Cyvin, Ed., Elsevier, Amsterdam, 1972.
(15) W. V. F. Brooks, M. Eshaque, C. Lau, and J. Passmore, *Can. J. Chem.*, **54**, 817 (1976).
(16) H. Oberhammer, *J. Chem. Phys.*, in press.
(17) J. Haase, *Z. Naturforsch. A*, **23**, 1000 (1968).
(18) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).
(19) A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, **17**, 2455 (1963).
(20) C. Glidwell, D. W. H. Rankin, A. G. Sheldrick, B. Beagley, and S. Cradock, *J. Chem. Soc. A*, 315 (1970).
(21) J. L. Hencher and S. H. Bauer, *Can. J. Chem.*, **51**, 2047 (1973).
(22) H. Burgi and L. S. Bartell, *J. Am. Chem. Soc.*, **94**, 5236 (1972).
(23) H. Oberhammer, O. Stelzer, and R. Schmutzler, *Inorg. Chem.*, in press.
(24) R. A. Crawford, F. B. Dudley, and K. Hedberg, *J. Am. Chem. Soc.*, **81**, 5287 (1959).
(25) R. B. Harvey and S. H. Bauer, *J. Am. Chem. Soc.*, **76**, 859 (1954).
(26) A. H. Clark and B. Beagley, *Trans. Faraday Soc.*, **67**, 2216 (1971).
(27) B. Csakvar, Z. Wagner, P. Gömöry, and F. C. Mijlhoff, *J. Organomet. Chem.*, **107**, 287 (1976).
(28) D. Käss and H. Oberhammer, *J. Mol. Struct.*, **40**, 65 (1977).
(29) F. C. Mijlhoff, *Recl. Trav. Chim. Pays-Bas*, **84**, 74 (1965).
(30) B. A. Arbuzov, V. A. Naumonv, N. M. Zaripov, L. D. Pronicheva, *Dokl. Akad. Nauk SSSR*, **195**, 1333 (1970).
(31) E. Z. Zasorin, J. M. Zharskii, G. P. Pinaev, V. N. Kupreev, and V. P. Spiridonov, *Zh. Strukt. Khim.*, **15**, 691 (1974).
(32) K. O. Christe, C. J. Schack, D. Philipovich, E. C. Curtis, and W. Sawodny, *Inorg. Chem.*, **12**, 620 (1973).
(33) E. Mayer and F. Sladky, *Inorg. Chem.*, **14**, 589 (1975).
(34) H. Braune and S. Knoke, *Z. Phys. Chem., Abt. B*, **21**, 297 (1933).
(35) L. O. Brockway and L. Pauling, *Proc. Natl. Acad. Sci. USA*, **19**, 68 (1933).
(36) V. C. Ewing and E. L. Sutton, *Trans. Faraday Soc.*, **59**, 1241 (1963).
(37) H. M. Seip and R. Stolevik, *Acta Chem. Scand.*, **20**, 1535 (1966).
(38) G. Gundersen and K. Hedberg in "Structure Data of Free Polyatomic Molecules", Landolt-Börnstein Group II, Vol. 7, Springer, West Berlin, 1976, p 77.