diphénique (Leser & Rabinovich, 1978) ce sont des interactions dipôle–dipôle ($^+$C=O$^-$) intramoléculaires qui imposent la conformation *syn* observée.

Enfin dans le cas du ADB il existe des liaisons hydrogène intermoléculaires du type N—H···O [N(7)···O^i(10′) = 3,064 (6) Å; N(7)—H(7)···O^i(10′) = 158 (4)° où O^i(10′) est en position $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$] responsables en partie de la cohésion cristalline. Un calcul des distances interatomiques entre les molécules du cristal fait ressortir de nombreux contacts dont les plus importants sont du type C···C [3,400 (7) Å], C···O [3,190 (5) Å] et C···H [2,88 (10) Å] qui assurent également la cohésion cristalline. Les liaisons hydrogène semblent être les seules en cause pour expliquer la conformation *syn* observée. Une analyse conformationnelle théorique menée à l'aide du programme *GENMOL* (Pèpe & Siri, 1990) pour le ADB, conduit à deux minima énergétiques correspondant aux deux conformations possibles *syn* et *anti*, mais avec une préférence pour le conformère *syn* de plus basse énergie.

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Références

Badr, M. Z. A., Aly, M. M., Fahmy, A. M. & Abdel-Latif, F. F. (1982). *Acta Chim. Acad. Sci. Hung.* **109**, 223–228.

Charbonneau, G. P. & Delugeard, Y. (1977). *Acta Cryst.* B**33**, 1586–1588.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* B**32**, 836–842.

Cruickshank, D. W. & Sparks, R. A. (1960). *Proc. R. Soc. London Ser. A*, **258**, 270–275.

Dewar, M. J. S. & Schmeising, H. N. (1959). *Tetrahedron*, **5**, 166–170.

Fronczek, F. R., Davis, S. T., Gehrig, L. M. B. & Gandour, R. D. (1987). *Acta Cryst.* C**43**, 1615–1618.

Johnson, C. K. (1965). *ORTEP*. Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee, EU.

Leser, J. & Rabinovich, D. (1978). *Acta Cryst.* B**34**, 2260–2263.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et de Louvain, Belgique.

Ottersen, T. (1977). *Acta Chem. Scand. Ser. A*, **31**, 480–484.

Pèpe, G. & Siri, D. (1990). *Stud. Phys. Theor. Chem.* **71**, 93–101.

Romming, C., Seip, H. M. & Aanesen Oymo, I.-M. (1974). *Acta Chem. Scand. Ser. A*, **28**, 507–514.

Sheldrick, G. M. (1976). *SHELX76*. Programme pour la détermination des structures cristallines. Univ. de Cambridge, Angleterre.

Shukla, A. P., Galy, A. M., Brouant, P., Galy, J. P., Soyfer, J. C. & Barbe, J. (1985). *Seventh International Symposium on Medicinal Chemistry, Proceedings*, Tome 2, pp. 213–214. Stockholm: Swedish Pharmaceutical Press.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Wasserman, H. J., Ryan, R. R. & Layne, S. P. (1985). *Acta Cryst.* C**41**, 783–785.

Acta Cryst. (1992). C**48**, 115–120

Structures of the Schiff-Base Ligands 1-[(1-Adamantylamino)methylene]-2(1*H*)-naphthalenone (1) and 1-[(2-Adamantylamino)methylene]-2(1*H*)-naphthalenone (2), and their Corresponding Copper(II) Complexes

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Abstract. (1) $C_{21}H_{23}NO$, M_r = 305·42, monoclinic, $P2_1/a$, a = 10·904 (3), b = 11·690 (3), c = 13·666 (2) Å, β = 111·72 (2)°, V = 1618 (1) Å^3, Z = 4, D_x = 1·25 g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 5·54 cm^{-1}, F(000) = 656, T = 296 K, R = 0·049 for 1632 unique observed reflections [$I > 3\sigma(I)$]. (2) $C_{21}H_{23}NO$, M_r = 305·42, monoclinic, $P2_1/c$, a = 6·513 (2), b = 10·554 (3), c = 23·455 (6) Å, β = 91·95 (3)°, V = 1611·1 (8) Å^3, Z = 4, D_x = 1·26 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·71 cm^{-1}, F(000) = 656, T = 296 K, R = 0·058 for 1722 unique observed reflections [$I > 3\sigma(I)$]. (I) Bis{(1-adamantyl)[(2-oxo-1*H*-naphth-1-ylidene)methyl]aminato}-copper(II), [Cu($C_{21}H_{22}NO$)$_2$], M_r = 672·38, monoclinic, $P2_1/a$, a = 18·139 (4), b = 10·227 (3), c = 19·543 (5) Å, β = 100·66 (2)°, V = 3563 (3) Å^3, Z = 4, D_x = 1·26 g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 11·14 cm^{-1}, F(000) = 1428, T = 296 K, R = 0·056 for 3381 unique observed reflections [$I > 3\sigma(I)$]. (II) Bis{(2-adamantyl)[(2-oxo-1*H*-naphth-1-ylidene)-

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methyl]aminato}copper(II), $[Cu(C_{21}H_{22}NO)_2]$, M_r = 672·38, triclinic, $P\bar{1}$, a = 11·854 (4), b = 13·688 (4), c = 10·530 (2) Å, α = 97·75 (2), β = 100·66 (2), γ = 104·80 (2)°, V = 1616 (2) Å^3, Z = 2, D_x = 1·34 g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 12·26 cm^{-1}, F(000) = 710, T = 296 K, R = 0·036 for 3498 unique observed reflections [$I > 3\sigma(I)$]. In the crystal state both ligands (1) and (2) are in the keto–amine tautomeric form. For the copper complexes (I) and (II), the geometry around the metal atom is distorted square planar, (I) being more distorted than (II). The angles between the chelate-ring planes in complexes (I) and (II) are 55·8 and 26·1°, respectively.

Introduction. Although metal Schiff-base complexes have been studied as reagents for oxygen separation and transport (Chen, Martell & Sun, 1989) and as models for biological dioxygen carriers (Henrici-Olivé & Olivé, 1974) or metalloenzymes (Spartalian, 1989; Kessissoglou, Butler & Pecoraro, 1987) there are still some stereochemical and conformational problems to solve for such species. For instance, it has been reported (Holm & O'Connor, 1971) that tetrahedral distortion is enhanced in bis(N-alkylsalicylaldaminato)copper complexes as the bulkiness of the radical bonded to the imine nitrogen increases. However, if we compare the complexes in the crystalline state when R = isopropyl (Orioli & Sacconi, 1966) and cyclohexyl (Tamura, Ogawa, Takeuchi & Yamada, 1977) we find that the geometry around the metal atom in the former is tetrahedrally distorted whereas in the lattter it is square planar. Furthermore, it is important to develop the available structural data of closely related systems, such as Schiff-base salicylaldamine and naphthaldamine complexes, and we have found that there are few X-ray crystal structures of naphthalenic Schiff-base copper compounds (Holm & O'Connor, 1971). Finally, in spite of the importance of Schiff bases and their complexes applied to biological problems, there are very few reports in the literature of correlations between the crystal structure of the ligands and their corresponding complexes (Bresciani Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio, 1976).

In this paper we report the single-crystal X-ray analysis of ligands (1) and (2) and their copper complexes (I) and (II) in order to compare possible differences in stereochemistry resulting from the isomerism of the ligands.

Experimental. The title compounds (ligands and complexes) were synthesized by known methods (Vogel, 1966; Yamada, Kuge & Yamagouchi, 1967). Crystals of (1) and (2) were grown by slow evaporation of MeOH while those of (I) and (II) were grown by diffusion of MeOH into a CH_2Cl_2 solution. The data for the four compounds were collected on a Nicolet $R3m$ four-circle diffractometer with either graphite-monochromated Mo $K\alpha$ (2) or Ni-filtered Cu $K\alpha$ [(1), (I) and (II)] radiation using an ω-scan mode with variable scan rate 4–30° min^{-1} and a scan width of 1·0°. Crystal data and additional data-collection parameters are given in Table 1.

Table 1. *Summary of data collection and structure refinement for* (1), (I), (2) *and* (II)

	(1)	(I)	(2)	(II)
Crystal size (mm)	0·15 × 0·13 × 0·34	0·14 × 0·2 × 0·4	0·22 × 0·36 × 0·34	0·14 × 0·2 × 0·38
No. of reflections for unit-cell determination	25	25	25	25
2θ range (°)	10·27–26·7	9·8–21·2	10·2–22	6·7–29
λ (Å)	1·54178	1·54178	0·71069	1·54178
$2\theta_{\min}$ (°)	3	3	3	3
$2\theta_{\max}$ (°)	110·1	110·1	50	110·1
No. of reflections measured	2298	4977	2857	4384
σ limit [$F > n\sigma(F)$], n	3	3	3	3
$R_{\rm merge}$	0·007975	0·019628	0·0497	0·027806
h	0, 11	−7, 7	0, 19	0, 12
k	0, 12	0, 12	0, 11	−14, 14
l	−14, 14	0, 26	−20, 20	−11, 11
Fluctuation of standard reflections (%)	0.5	0.1	1.2	2.0
Absorption correction	—	ψ	—	*DIFABS*
Max., min. transmission factors	—	1·000 0·5961	—	1·1481 0·8645
wR	0·067	0·078	0·057	0·057
Max. Δ/σ	0·01	0·01	0·045	0·003
Largest peak in final difference map (e Å^{-3})	0·19	1·15	0·20	0·35
Deepest hole (e Å^{-3})	−0·19	−0·53	−0·20	−0·36
Weighting scheme	$1/\sigma$	$1/\sigma$	$1/\sigma$	$1/\sigma$
S	1.44	1.66	1.17	1.39

The structures were solved by direct methods and subsequent Fourier difference maps. They were refined by full-matrix least-squares methods (on F) using anisotropic thermal parameters for all non-H atoms. The H atoms of CH and CH_2 groups were allowed to ride on bonded C atoms. The H atoms bonded to N atoms were found on a difference Fourier map at an advanced stage of refinement and their coordinates were refined.

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Solution and refinement of (2) was carried out by using *SHELXTL* (Sheldrick, 1981) on a Nova 4S computer, while (1), (I) and (II) were solved and refined on a VAX station II using *TEXSAN* (Molecular Structure Corporation, 1985). Data for (I) and (II) were corrected for absorption using the ψ-scan method and *DIFABS* (Walker & Stuart, 1983), respectively.

Table 2. *Positional parameters and equivalent isotropic thermal parameters* (Å^2) *for compounds* (1), (2), (I) *and* (II)

For compounds (1), (I) and (II) the equivalent isotropic thermal parameter is defined as $B_{eq} = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$. For compound (2) equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	B_{eq}/U_{eq}
(1)				
O1*A*	0·7985 (2)	−0·1389 (1)	0·2656 (1)	4·02 (8)
N1*A*	0·6692 (2)	−0·3186 (2)	0·2788 (1)	3·23 (8)
C1*A*	0·5638 (2)	−0·1485 (2)	0·1904 (2)	2·8 (1)
C2*A*	0·6869 (2)	−0·899 (2)	0·2178 (2)	3·2 (1)
C3*A*	0·6842 (2)	0·0300 (2)	0·1924 (2)	3·8 (1)
C4*A*	0·5699 (3)	0·0845 (2)	0·1411 (2)	3·9 (1)
C5*A*	0·3276 (3)	0·0866 (2)	0·0527 (2)	4·3 (1)
C6*A*	0·2084 (3)	0·0321 (2)	0·0175 (2)	4·5 (1)
C7*A*	0·2036 (3)	−0·0836 (2)	0·0366 (2)	4·2 (1)
C8*A*	0·3164 (2)	−0·1438 (2)	0·0926 (2)	3·6 (1)
C9*A*	0·4452 (2)	0·0282 (2)	0·1079 (2)	3·4 (1)
C10*A*	0·4409 (2)	−0·0899 (2)	0·1302 (2)	3·0 (1)
C11*A*	0·5618 (2)	−0·2612 (2)	0·2260 (2)	3·0 (1)
C12*A*	0·6774 (2)	−0·432 (2)	0·3263 (2)	2·9 (1)
C13*A*	0·8179 (2)	−0·4755 (2)	0·3512 (2)	3·8 (1)
C14*A*	0·8350 (3)	−0·5930 (2)	0·4039 (2)	4·2 (1)
C15*A*	0·7375 (3)	−0·6771 (2)	0·3282 (2)	4·7 (1)
C16*A*	0·5975 (3)	−0·6352 (2)	0·3035 (2)	4·0 (1)
C17*A*	0·5700 (3)	−0·6268 (2)	0·4051 (2)	4·4 (1)
C18*A*	0·6671 (3)	−0·5434 (2)	0·4801 (2)	4·0 (1)
C19*A*	0·6493 (2)	−0·4249 (2)	0·4281 (2)	3·6 (1)
C20*A*	0·5793 (2)	−0·5166 (2)	0·2511 (2)	3·7 (1)
C21*A*	0·8075 (3)	−0·5838 (2)	0·5053 (2)	4·4 (1)
(2)				
O1*A*	0·7684 (3)	0·1942 (2)	0·07713 (1)	60 (1)
N1*A*	0·4012 (4)	0·2676 (2)	0·0469 (1)	50 (1)
C1*A*	0·5795 (4)	0·3248 (3)	0·1340 (1)	41 (1)
C2*A*	0·7568 (4)	0·2538 (3)	0·1189 (1)	46 (1)
C3*A*	0·9284 (4)	0·2494 (3)	0·1588 (1)	53 (1)
C4*A*	0·9274 (4)	0·3139 (3)	0·2086 (1)	57 (1)
C5*A*	0·7637 (5)	0·4595 (3)	0·2751 (1)	65 (1)
C6*A*	0·6016 (6)	0·5324 (4)	0·2904 (1)	74 (1)
C7*A*	0·4275 (5)	0·5384 (1)	0·2548 (1)	67 (1)
C8*A*	0·4163 (4)	0·4714 (3)	0·2044 (1)	53 (1)
C9*A*	0·7568 (5)	0·3899 (3)	0·2242 (1)	51 (1)
C10*A*	0·5808 (4)	0·3951 (3)	0·1872 (1)	42 (1)
C11*A*	0·4090 (4)	0·3268 (3)	0·0953 (1)	45 (1)
C12*A*	0·2728 (4)	0·3792 (3)	−0·0389 (1)	47 (1)
C13*A*	0·2312 (4)	0·2748 (3)	0·0046 (1)	48 (1)
C14*A*	0·2013 (4)	0·1492 (3)	−0·0262 (1)	51 (1)
C15*A*	0·00131 (4)	0·1603 (3)	−0·0670 (1)	58 (1)
C16*A*	0·0490 (4)	0·2640 (3)	−0·1107 (1)	55 (1)
C17*A*	0·2395 (5)	0·2332 (3)	−0·1445 (1)	59 (1)
C18*A*	0·4270 (4)	0·2216 (3)	−0·1041 (1)	50 (1)
C19*A*	0·4612 (4)	0·3461 (3)	−0·0725 (1)	49 (1)
C20*A*	0·0842 (4)	0·3899 (3)	−0·0797 (1)	58 (1)
C21*A*	0·3901 (4)	0·1170 (3)	−0·0606 (1)	54 (1)
(I)				
Cu	0·76029 (3)	0·22574 (6)	0·75790 (3)	3·48 (3)
O1*A*	0·6640 (2)	0·2058 (3)	0·7809 (2)	4·2 (1)
N1*A*	0·7330 (2)	0·1300 (3)	0·6679 (2)	3·1 (1)
C1*A*	0·6046 (2)	0·0770 (4)	0·6849 (2)	3·1 (2)
C2*A*	0·6063 (2)	0·1422 (4)	0·7480 (2)	3·2 (2)
C3*A*	0·5408 (3)	0·1395 (5)	0·7798 (2)	3·9 (2)
C4*A*	0·4802 (3)	0·0732 (5)	0·7521 (2)	4·1 (2)
C5*A*	0·4112 (2)	−0·0712 (5)	0·6613 (3)	4·2 (2)
C6*A*	0·4058 (3)	−0·1396 (5)	0·6014 (3)	4·5 (2)
C7*A*	0·4653 (3)	−0·1350 (5)	0·5654 (3)	4·6 (2)
C8*A*	0·5299 (2)	−0·0653 (5)	0·5912 (2)	4·0 (2)
C9*A*	0·4755 (2)	0·0009 (4)	0·6895 (2)	3·4 (2)
C10*A*	0·5380 (2)	0·0051 (4)	0·6535 (2)	3·1 (2)
C11*A*	0·6671 (2)	0·0795 (4)	0·6486 (2)	3·2 (2)
C12*A*	0·7883 (2)	0·1195 (4)	0·6188 (2)	3·0 (2)
C13*A*	0·8451 (2)	0·0115 (4)	0·6451 (2)	3·9 (2)
C14*A*	0·9049 (3)	0·0075 (5)	0·5979 (3)	4·5 (2)
C15*A*	0·9452 (3)	0·1381 (6)	0·6011 (3)	5·1 (3)
C16*A*	0·8891 (3)	0·2255 (5)	0·5742 (3)	4·5 (2)
C17*A*	0·8515 (3)	0·2172 (5)	0·4994 (3)	4·7 (2)
C18*A*	0·8119 (3)	0·0857 (5)	0·4979 (2)	3·8 (2)
C19*A*	0·7523 (3)	0·0904 (4)	0·5439 (2)	3·6 (2)
C20*A*	0·8292 (3)	0·2518 (4)	0·6204 (2)	3·7 (2)
C21*A*	0·8679 (3)	−0·0212 (5)	0·5235 (3)	4·3 (2)
O1*B*	0·8603 (2)	0·1665 (3)	0·7873 (2)	4·4 (1)
N1*B*	0·7794 (2)	0·3877 (3)	0·8121 (2)	3·4 (1)
C1*B*	0·8853 (2)	0·2931 (4)	0·8929 (2)	3·3 (2)
C2*B*	0·8996 (3)	0·1905 (4)	0·8495 (2)	3·7 (2)
C3*B*	0·9618 (3)	0·1072 (5)	0·8725 (3)	4·5 (2)
C4*B*	1·0065 (3)	0·1214 (6)	0·9356 (3)	5·0 (2)
C5*B*	1·0370 (3)	0·2329 (6)	1·0499 (3)	5·6 (3)
C6*B*	1·0206 (4)	0·3261 (8)	1·0946 (6)	6·5 (3)
C7*B*	0·9603 (4)	0·4071 (6)	1·0752 (3)	5·8 (3)
C8*B*	0·9164 (3)	0·3980 (5)	1·0106 (2)	4·9 (2)
C9*B*	0·9925 (3)	0·2204 (5)	0·9824 (2)	4·4 (2)
C10*B*	0·9302 (3)	0·3066 (4)	0·9615 (2)	3·8 (2)
C11*B*	0·8305 (2)	0·3908 (5)	0·8685 (2)	3·6 (2)
C12*B*	0·7305 (2)	0·5066 (4)	0·7936 (2)	3·4 (2)
C13*B*	0·6702 (3)	0·5136 (5)	0·8404 (3)	4·5 (2)
C14*B*	0·6181 (3)	0·6312 (6)	0·8164 (3)	5·5 (3)
C15*B*	0·5805 (3)	0·6159 (6)	0·7412 (3)	5·8 (3)
C16*B*	0·6396 (3)	0·6077 (5)	0·6959 (3)	5·3 (3)
C17*B*	0·6876 (3)	0·7337 (6)	0·7035 (3)	5·6 (3)
C18*B*	0·7238 (3)	0·7506 (5)	0·7788 (3)	5·4 (3)
C19*B*	0·7751 (3)	0·6348 (5)	0·8022 (3)	4·3 (2)
C20*B*	0·6915 (3)	0·4933 (5)	0·7180 (2)	4·1 (2)
C21*B*	0·6643 (4)	0·7579 (6)	0·8237 (3)	6·1 (3)
(II)				
Cu	0·03641 (3)	0·21379 (3)	0·18579 (3)	2·89 (2)
O1*A*	−0·1076 (2)	0·1316 (1)	0·0840 (2)	3·73 (7)
N1*A*	0·0848 (2)	0·0917 (2)	0·2307 (2)	2·61 (7)
C1*A*	−0·0988 (2)	−0·0362 (2)	0·1183 (2)	2·68 (8)
C2*A*	−0·1577 (2)	0·0338 (2)	0·0766 (2)	2·9 (1)
C3*A*	−0·2793 (2)	−0·0043 (2)	0·0199 (3)	3·5 (1)
C4*A*	−0·3388 (2)	−0·1046 (2)	0·0078 (3)	3·7 (1)
C5*A*	−0·3456 (2)	−0·2816 (2)	0·0372 (3)	4·1 (1)
C6*A*	−0·2927 (3)	−0·3517 (2)	0·0742 (3)	4·6 (1)
C7*A*	−0·1723 (3)	−0·3202 (2)	0·1241 (3)	4·2 (1)
C8*A*	−0·1077 (2)	−0·2201 (2)	0·1369 (3)	3·6 (1)
C9*A*	−0·2830 (2)	−0·1772 (2)	0·0471 (3)	3·2 (1)
C10*A*	−0·1606 (2)	−0·1440 (2)	0·1008 (2)	3·0 (1)
C11*A*	0·0211 (2)	−0·0017 (2)	0·1854 (2)	2·7 (1)
C12*A*	0·2497 (2)	0·0160 (2)	0·3240 (2)	2·87 (9)
C13*A*	0·2043 (2)	0·1095 (2)	0·3058 (2)	2·52 (8)
C14*A*	0·2142 (2)	0·1743 (2)	0·4393 (3)	3·1 (1)
C15*A*	0·3464 (2)	0·2163 (2)	0·4968 (3)	3·6 (1)
C16*A*	0·3991 (2)	0·1268 (2)	0·5111 (3)	3·8 (1)
C17*A*	0·3368 (3)	0·0649 (3)	0·6063 (3)	4·3 (1)
C18*A*	0·2048 (3)	0·0231 (2)	0·5511 (3)	3·9 (1)
C19*A*	0·1899 (2)	−0·0476 (2)	0·4192 (3)	3·6 (1)
C20*A*	0·3818 (2)	0·0582 (2)	0·3802 (3)	3·5 (1)
C21*A*	0·1506 (2)	0·1089 (2)	0·5303 (3)	3·8 (1)
O1*B*	0·1938 (2)	0·2989 (1)	0·2267 (2)	3·66 (7)
N1*B*	−0·0259 (2)	0·3352 (2)	0·1983 (2)	2·77 (7)
C1*B*	0·1621 (2)	0·4599 (2)	0·1932 (2)	2·69 (9)
C2*B*	0·2341 (2)	0·3958 (2)	0·2217 (3)	3·0 (1)
C3*B*	0·3594 (2)	0·4388 (2)	0·2511 (3)	3·5 (1)
C4*B*	0·4105 (2)	0·5371 (2)	0·2458 (3)	3·6 (1)
C5*B*	0·3974 (2)	0·7074 (2)	0·2049 (3)	3·5 (1)
C6*B*	0·3318 (3)	0·7721 (2)	0·1715 (3)	4·0 (1)
C7*B*	0·2103 (3)	0·7345 (2)	0·1405 (3)	3·9 (1)
C8*B*	0·1537 (2)	0·6347 (2)	0·1460 (3)	3·4 (1)
C9*B*	0·3421 (2)	0·6041 (2)	0·2104 (2)	3·0 (1)
C10*B*	0·2175 (2)	0·5661 (2)	0·1827 (2)	2·78 (9)
C11*B*	0·0369 (2)	0·4260 (2)	0·1893 (2)	2·8 (1)
C12*B*	−0·2078 (2)	0·4073 (2)	0·2096 (3)	3·0 (1)
C13*B*	−0·1542 (2)	0·3162 (2)	0·2047 (2)	2·77 (9)
C14*B*	−0·1845 (2)	0·2622 (2)	0·3211 (3)	3·7 (1)
C15*B*	−0·3184 (3)	0·2183 (2)	0·3025 (3)	4·3 (1)
C16*B*	−0·3776 (2)	0·3045 (2)	0·2999 (3)	4·0 (1)
C17*B*	−0·3373 (3)	0·3784 (3)	0·4289 (3)	5·2 (1)
C18*B*	−0·2034 (3)	0·4234 (3)	0·4488 (3)	5·0 (1)
C19*B*	−0·1689 (3)	0·4816 (2)	0·3393 (3)	4·1 (1)
C20*B*	−0·3421 (2)	0·3626 (2)	0·1900 (3)	3·7 (1)
C21*B*	−0·1410 (3)	0·3380 (3)	0·4482 (3)	4·8 (1)

Discussion. Final positional parameters for compounds (1), (2), (I) and (II) are given in Table 2.* Tables 3 and 4 contain bond lengths and selected bond angles. The molecular structures of the compounds including atom-numbering schemes, are illustrated in Figs. 1–4.

Compounds (1) and (2) (Figs. 1 and 2) are structurally very similar. In both ligands the tautomeric keto–amine form is observed, with N—H distances of 0·93 (2) and 0·90 (5) Å respectively. The corresponding O···H distances are 1·79 (2) and 1·76 (3) Å and the O···H—N angles are 140·4 (6) and 145·3 (8)° respectively. Bond lengths in the molecule suggest an electronic delocalization in the N1—C11—C1—C2—O1 bonds. C2—O1 bond lengths [1·283 (3) and 1·286 (3) Å] are similar to the values observed for conjugated C=O bonds while the corresponding bond in Schiff bases derived from salicylaldehyde, which in the solid state are in the enol–imine tautomeric form, have bond lengths in the range 1·34 (2)–1·36 (9) Å (Moustakali-Mavridis, Hadjoudis & Mavridis, 1978, 1980).

The C11—N1 distances for (1) and (2) [1·310 (3) and 1·294 (4) Å, respectively] have values in the same range as those observed in compounds with C=N nonconjugated double bonds (Sandorfy, 1970). The C1—C2 bond has a very similar length in both compounds [1·428 (3) and 1·431 (4) Å] and follows the trend for the remaining C—C bonds in the naphthalene moiety. Nevertheless, the C3—C4 bond is the shortest in the naphthalene ring [1·342 (4) and 1·352 (4) Å], which is in agreement with the quinonoid character of the compounds (Näsäkkälä, Saarinen, Korvenranta & Näsäkkälä, 1977). All bonds in the adamantane group have distances in the normal ranges of C—C and C—N bond lengths.

As expected the ligands undergo some changes upon coordination, with a shortening of C1—C2 and a lengthening of the C1—C11 in each case. The other bond that changes significantly upon coordination is N1—C12 in the case of compounds (1) and (I) and N(1)—C(13) in the case of (2) and (II). The changes are slightly greater on going from (1) to (2) than on going from (I) to (II) particularly in the N1—C12 bond, *i.e.* the bond that joins the N atom and the adamantane fragment. Note that the bond is longer when the N atom is bonded to a tertiary C atom in the adamantane radical.

Table 3. *Bond lengths* (Å) *for compounds* (1), (I), (2) *and* (II)

	(1)	(I) *A*	(I) *B*	(2)	(II) *A*	(II) *B*
Cu—O1*A*	—	1·893 (3)		—	1·894 (2)	
Cu—N1*A*	—	1·994 (3)		—	1·996 (2)	
Cu—O1*B*	—	1·898 (3)		—	1·896 (2)	
Cu—N1*B*	—	1·962 (4)		—	1·979 (2)	
N1—C11	1·310 (3)	1·293 (5)	1·303 (5)	1·294 (4)	1·296 (3)	1·296 (3)
N1—C12	1·476 (3)	1·515 (5)	1·509 (5)	—	—	—
N1—C13	—	—	—	1·463 (4)	1·484 (3)	1·487 (3)
O1—C2	1·283 (3)	1·297 (5)	1·315 (5)	1·286 (3)	1·305 (3)	1·301 (3)
C1—C2	1·428 (3)	1·397 (6)	1·403 (6)	1·431 (4)	1·408 (4)	1·408 (4)
C1—C11	1·408 (3)	1·443 (6)	1·428 (6)	1·411 (4)	1·440 (4)	1·431 (4)
C2—C3	1·442 (3)	1·440 (6)	1·419 (6)	1·434 (4)	1·427 (4)	1·430 (4)
C3—C4	1·342 (4)	1·321 (6)	1·353 (7)	1·352 (4)	1·355 (4)	1·338 (4)
C4—C9	1·425 (3)	1·418 (6)	1·418 (8)	1·428 (4)	1·406 (4)	1·429 (4)
C9—C5	1·402 (3)	1·404 (6)	1·420 (7)	1·402 (4)	1·416 (4)	1·410 (4)
C5—C6	1·365 (4)	1·352 (7)	1·360 (1)	1·364 (4)	1·347 (5)	1·373 (4)
C6—C7	1·381 (4)	1·392 (7)	1·369 (9)	1·386 (5)	1·396 (4)	1·383 (4)
C7—C8	1·378 (3)	1·385 (6)	1·366 (7)	1·377 (4)	1·368 (4)	1·372 (4)
C8—C10	1·410 (3)	1·399 (6)	1·396 (7)	1·410 (4)	1·417 (4)	1·412 (4)
C9—C10	1·418 (3)	1·442 (6)	1·431 (7)	1·414 (4)	1·426 (4)	1·415 (4)
C1—C10	1·458 (3)	1·450 (6)	1·440 (6)	1·452 (4)	1·446 (4)	1·459 (4)
C12—C13	1·523 (3)	1·534 (6)	1·552 (6)	1·533 (4)	1·536 (3)	1·535 (3)
C13—C14	1·530 (3)	1·549 (6)	1·548 (7)	1·520 (4)	1·532 (4)	1·545 (4)
C14—C15	1·534 (4)	1·519 (7)	1·508 (8)	1·520 (4)	1·542 (4)	1·526 (4)
C15—C16	1·518 (4)	1·523 (8)	1·514 (8)	1·523 (4)	1·527 (4)	1·521 (4)
C16—C17	1·529 (4)	1·522 (8)	1·547 (8)	1·530 (4)	1·533 (4)	1·526 (5)
C17—C18	1·522 (4)	1·523 (7)	1·506 (8)	1·525 (4)	1·534 (4)	1·526 (5)
C18—C19	1·535 (3)	1·529 (6)	1·523 (7)	1·533 (4)	1·545 (4)	1·524 (5)
C12—C19	1·535 (3)	1·517 (6)	1·534 (6)	1·521 (4)	1·534 (4)	1·532 (4)
C12—C20	1·529 (3)	1·541 (6)	1·521 (6)	1·535 (4)	1·538 (4)	1·531 (4)
C16—C20	1·539 (3)	1·538 (7)	1·514 (7)	1·528 (4)	1·519 (4)	1·529 (4)
C18—C21	1·516 (4)	1·513 (7)	1·514 (8)	1·527 (4)	1·505 (4)	1·534 (5)
C14—C21	1·516 (4)	1·512 (7)	1·525 (8)	1·532 (4)	1·532 (4)	1·525 (5)
N1—H1	0·93 (2)	—	—	0·90 (5)	—	—

Table 4. *Selected bond angles* (°) *in compounds* (1), (I), (2) *and* (II)

	(1)	(I) *A*	(I) *B*	(2)	(II) *A*	(II) *B*
N1*A*—Cu—N1*B*		151·7 (1)			161·30 (9)	
N1*A*—Cu—O1*B*		100·2 (1)			92·4 (9)	
N1*A*—Cu—O1*A*		93·8 (1)			92·58 (8)	
O1*A*—Cu—O1*B*		140·0 (2)			159·3 (1)	
O1*A*—Cu—N1*B*		92·4 (1)			90·71 (8)	
O1*B*—Cu—N1*B*		92·5 (1)			90·98 (8)	
Cu—N1—C11		121·3 (3)	120·3 (3)		122·4 (2)	123·1 (2)
Cu—N1—C12		120·5 (2)	120·9 (3)		—	—
Cu—N1—C13		—	—		117·7 (2)	116·5 (2)
C2—O1—Cu		129·2 (3)	123·0 (3)		128·9 (2)	129·2 (2)
O1—C2—C1	122·9 (2)	124·1 (4)	124·8 (4)	122·9 (2)	124·2 (2)	124·0 (2)
C11—C1—C2	119·4 (2)	122·3 (4)	121·1 (4)	118·2 (2)	121·0 (2)	120·9 (2)
C11—N1—C12	127·1 (2)	118·2 (3)	118·5 (4)	—	—	—
C11—N1—C13	—	—	—	125·1 (2)	119·4 (2)	120·1 (2)
N1—C11—C1	123·0 (2)	129·1 (4)	127·4 (4)	124·3 (3)	128·5 (2)	127·5 (2)

Complexes (I) and (II) (Figs. 3 and 4) also have very similar structures. In both cases the Cu ion is bonded to the O and N donor atoms of the two ligand molecules in a *trans* arrangement. For each complex, the two Cu—O bonds have similar lengths while the Cu—N distances are different for each ligand. On the other hand, the values for Cu—O and Cu—N bond lengths are similar to those observed in several salicylidenaminato copper complexes (Bhatia, Bindlish, Saini & Jain, 1981; Panattoni, Bombieri & Graziani, 1967; Hall, Summer & Waters, 1969). To our knowledge there are very few reports on the structure of (1,2-naphthaldaminato)copper complexes (Clark, Waters & Williams, 1977; Clark, Waters & Waters, 1975; Martin & Waters, 1973; Shnulin, Mamedov & Struchkov, 1978). Cu—O distances in those complexes range from 1·87 to 1·92 Å

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* Lists of structure factors, complete bond lengths and angles, least-squares planes, anisotropic thermal parameters, H-atom parameters, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54391 (70 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

while Cu—N distances have values between 1·971 and 2·013 Å. The values observed in (I) and (II) are thus intermediate. The C1—C2 bond length is also similar in the two complexes.

Bond angles in complexes (I) and (II) show that the coordination geometry about the Cu atoms is distorted square planar. The distortion is larger in (I) than in (II) with O—Cu—O angles of 140·0 (2) and 159·3 (1)°, respectively. Other angles in the ligands show expected values.

The distortion from planarity is also greater in the complex with ligand (1), suggesting that the amount of substitution on the C atom bonded to the imine N atom may also affect the degree of distortion. However, although the 2-adamantyl radical is bulkier than the isopropyl one, if we compare distortion in the solid state between bis(*N*-isopropylsalicylidenaminato)copper(II) (Orioli & Sacconi, 1966) and bis(*N*-isopropyl-2-oxo-1-naphthylidenaminato)-copper(II) (Matsumoto, Nonaka, Kida, Kawano & Ueda, 1979) with (II), we can observe that (II) is less distorted because the angles between the two chelate-ring planes are 59·7, 38·6 and 26·1°, respectively. Finally, the changes in the Cu—N distances on going from one ligand molecule to the other one in the same complex are larger in (I) than in (II), and this effect may also be related to the greater distortion from planarity.

In complex (I) the plane formed by Cu—N1*A*—C11*A*—C1*A*—C2*A*—O*A* (plane 1) is nearly coplanar with the neighbouring naphthalene moiety (plane 2). The angle between the two least-squares planes is 4·1°. However, the planarity is broken on the other side of the molecule. The coordination ring formed by the other ligand, atoms labeled *B* (plane 3), exhibits a large deviation from planarity. The resulting 'plane' forms angles of 124·2 and 121·9° with planes 1 and 2 respectively. The naphthalene fragment of the ligand (plane 4) forms an angle of 12·4°

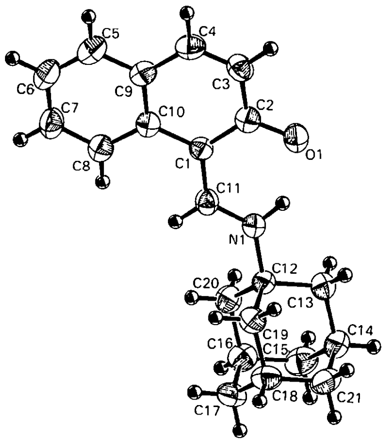

Fig. 1. *ORTEP* diagram of compound (1) drawn at 50% probability.

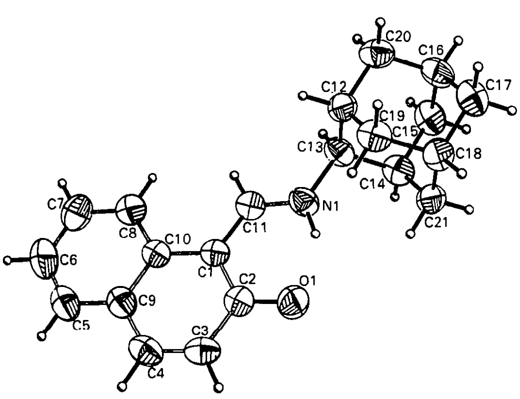

Fig. 2. *ORTEP* diagram of compound (2) drawn at 50% probability.

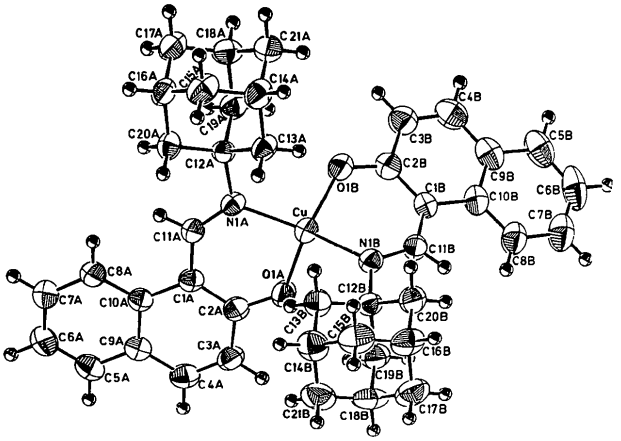

Fig. 3. *ORTEP* diagram of compound (I) drawn at 50% probability.

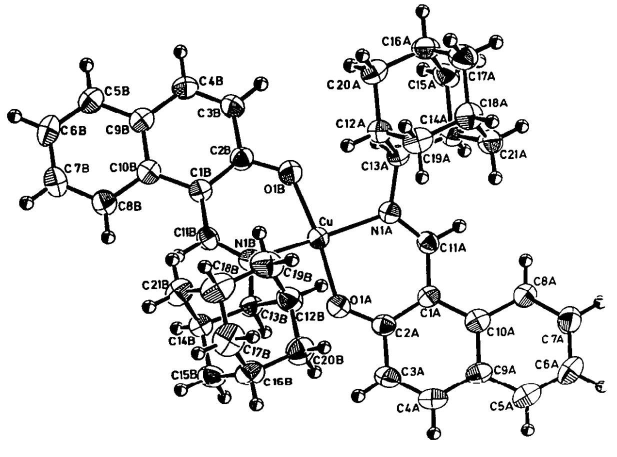

Fig. 4. *ORTEP* diagram of compound (II) drawn at 50% probability.

with the coordination plane 3, so the whole ligand itself is not planar.

There are some differences in complex (II), and in each ligand the chelate (1 and 3 planes) and the naphthalene rings (2 and 4 planes) form an angle of about 10°. The angle between the two coordination planes is 153·9°.

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References

Bhatia, S. C., Bindlish, J. M., Saini, A. R. & Jain, P. C. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1773–1779.

Bresciani Pahor, N., Calligaris, M., Delise, P., Dodic, G., Nardin, G. & Randaccio, L. (1976). *J. Chem. Soc. Dalton Trans.* pp. 2478–2483.

Chen, D., Martell, A. E. & Sun, Y. (1989). *Inorg. Chem.* **28**, 2647–2652.

Clark, G. R., Waters, J. M. & Waters, T. N. (1975). *J. Inorg. Nucl. Chem.* **37**, 2455–2458.

Clark, G. R., Waters, T. N. & Williams, G. J. (1977). *J. Inorg. Nucl. Chem.* **39**, 1971–1975.

Hall, D., Summer, R. H. & Waters, T. N. (1969). *J. Chem. Soc. A*, pp. 420–422.

Henrici-Olivé, G. & Olivé, S. (1974). *Angew. Chem. Int. Ed. Engl.* **13**, 29–38.

Holm, R. H. & O'Connor, M. J. (1971). *Prog. Inorg. Chem.* **14**, 241–401.

Kessissoglou, D. P., Butler, W. M. & Pecoraro, V. L. (1987). *Inorg. Chem.* **26**, 495–503.

Martin, D. W. & Waters, T. N. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2440–2443.

Matsumoto, N., Nonaka, Y., Kida, S., Kawano, S. & Ueda, I. (1979). *Inorg. Chim. Acta*, **37**, 27–36.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Moustakali-Mavridis, I., Hadjoudis, E. & Mavridis, A. (1978). *Acta Cryst.* B**34**, 3709–3715.

Moustakali-Mavridis, I., Hadjoudis, E. & Mavridis, A. (1980). *Acta Cryst.* B**36**, 1126–1130.

Näsäkkälä, M., Saarinen, H., Korvenranta J. & Näsäkkälä, E. (1977). *Acta Chem. Scand. Ser. A*, **31**, 469–472.

Orioli, P. L. & Sacconi, L. (1966). *J. Am. Chem. Soc.* **88**, 277–280.

Panattoni, C., Bombieri, G. & Graziani, R. (1967). *Acta Cryst.* **23**, 537–544.

Sandorfy, C. (1970). *The Chemistry of the Carbon–Nitrogen Double Bond*, edited by S. Patai, p. 2. London: Interscience.

Sheldrick, G. M. (1981). *SHELXTL Version* 3. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Germany.

Shnulin, A. N., Mamedov, Kh. S. & Struchkov, Yu. T. (1978). *Zh. Strukt. Khim.* **19**, 686–688.

Spartalian, K. (1989). *Inorg. Chem.* **28**, 19–24.

Tamura, H., Ogawa, K., Takeuchi, A. & Yamada, S. (1977). *Chem. Lett.* pp. 889–890.

Vogel, A. I. (1966). *Practical Organic Chemistry*, pp. 653–654. London: Longmans.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Yamada, S., Kuge, K. & Yamagouchi, K. (1967). *Bull Chem. Soc. Jpn*, **40**, 1864–1867.

Acta Cryst. (1992). C**48**, 120–123

Structure of 2,4:3,5-Di-*O*-isopropylidene-D-mannitol

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Abstract. $C_{12}H_{22}O_6$, M_r = 262·302, monoclinic, $P2_1$, a = 11·389 (3), b = 11·617 (3), c = 12·061 (3) Å, β = 115·33 (2)°, V = 1442·3 Å^3, Z = 4, D_x = 1·208 g cm^{-3}, m.p. = 407–409 K, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·90 cm^{-1}, $F(000)$ = 568, T = 292 K, final R = 0·039 for 1458 observed reflections. There are no strong conformational differences between the two symmetry-independent molecules, the dioxane rings are all in the twist-boat conformation. Each of the molecules is nearly symmetric with respect to a pseudo-twofold axis perpendicular to the C(3)—C(4) bond. The molecules are linked into sheets parallel to crystal plane (100) by hydrogen bonds between the hydroxyl groups. There are four symmetry-independent hydrogen bonds in this structure [2·758 (8), 2·699 (5), 2·644 (7), 2·640 (8) Å] and they form one eight-membered ring. Intramolecular hydrogen bonds also occur between the hydroxyl groups and dioxane oxygens in accordance with the results of a ^{13}C NMR study of this compound in solution.

Introduction. 2,4:3,5-Di-*O*-isopropylidene-D-mannitol [hereinafter referred to as (I)] was obtained, together with the 2,3:4,5-derivative, from 1,6-di-*O*-benzoyl-D-mannitol by Gawrońska (1988). The structures of both were established by ^{13}C NMR spectroscopy. Small $\Delta\delta$ values, of 1 p.p.m., for the ^{13}C NMR reso-

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