Preparation and molecular structure of an adipinato copper norbornadiene complex *

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(Received March 12, 1993)

Abstract

Adipinato(bicyclo[2.2.1]-hepta-2,5-diene)bis(pyridine)dicopper(I) pyridine was obtained by the reaction of adipinatodicopper(I) with bicyclo[2.2.1]-hepta-2,5-diene in pyridine, and its structure determined by an X-ray diffraction study. It forms a zigzag chain, with the two carboxylate groups of the adipinate ligand coordinated to copper(I) in a monodentate fashion. A pyridine molecule is also attached to each copper. Both double bonds of the olefin are coordinated to copper atoms in an *exo* configuration, so that the olefin forms a cross-link between two copper adipinate chains. Both copper atoms have a trigonal planar geometry, and molecules are linked by alternating adipinate and norbornadiene chelates to give a polymeric structure.

1. Introduction

Solutions of copper salts have been used for the extraction of olefins from gaseous mixtures (see for example ref. 1). Some copper(I) complexes promote the valence isomerization of bicyclo[2.2.1]-hepta-2,5-diene (norbornadiene (NBD)) to quadricyclene (quadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane) [2]. Furthermore copper probably plays a role at the receptor site for binding the plant hormone ethylene [3]. Polyolefin complexes of copper(I) salts are of moderate stability in the solid state, most of these complexes isolated involving coordinated halide [4].

NBD forms a great number of metal complexes as either a monodentate or a bidentate ligand. Copper halides form 1:1 and 2:1 complexes with NBD [5–8]. The 1:2 complexes are tetrameric and in the 2:1

complexes the NBD is fully coordinated. In the NBD complex of copper(I) acetate NBD seems to act as a chelating ligand [9,10]. As part of our study of the reactions of dinuclear copper(I) complexes with various small molecules that we examined the reaction of copper(I) adipinate with olefins and with diolefins in the hope of obtaining stable compounds for structural studies. Only in the case of NBD were we able to isolate a polymeric copper(I) adipinate complex.

2. Experimental details

2.1. Preparation of adipinatobis(pyridine)copper(II)

To a solution of adipic acid (29.2 g, 200 mmol) in ethanol (35 ml) was added one of copper(II) acetate (40 g, 200 mmol) in ethanol (1200 ml). The blue complex was filtered off, dried gently in the air and then stirred with pyridine (500 ml) for 4 h. The blue complex formed was filtered off, dried in vacuum and shown to be the title compound (yield, 62.2 g (85%)). Elemental anal. Found: C, 47.05; H, 4.15; N, 6.39; Cu,

29.3. $C_{16}H_{18}N_2O_4Cu_2$ (429.42) calc.: C, 47.75; H, 4.22; N, 6.53; Cu, 29.60%. IR (KBr): $\nu(CO_2)_{as}$ 1602, $\nu(CO_2)_s$ 1445 cm^{-1}.

2.2. Preparation of [(CH$_2$CH$_2$CO$_2$Cu)$_2$(NBD)(py)$_2$·py]

A mixture of adipinatobis(pyridine)copper(II) (1.0 g, 2.75 mmol), copper powder (0.39 g, 6.14 mmol) and pyridine (10 ml) was refluxed under argon for 3 h. The originally blue solution turned yellow. The excess of copper was removed by filtration and NBD (0.5 ml, 4.7 mmol) was added to the filtrate causing immediate separation of colourless crystals. After this had been stood overnight, more crystals in the form of prisms were formed. The solid was filtered off, washed twice with ether, dried in vacuum and shown to be [(CuO$_2$CCH$_2$CH$_2$)$_2$(NBD)(py)$_2$·py] (yield, 0.984 g (59.6%)). The crystals which are extremely air sensitive were suitable for an X-ray structure determination.

2.3. Determination of crystal structure

A crystal of the approximate dimensions 0.15 mm × 0.15 mm × 0.50 mm was selected under protection with dry argon. The unit-cell parameters were determined and X-ray intensity data were collected on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator using Cu Kα radiation. Lattice parameters were obtained by least-squares fit for 25 reflections in the range $23° \leqslant \theta \leqslant 26°$, two octants $(0 \leqslant h \leqslant 12; 0 \leqslant k \leqslant 22; -19 \leqslant l \leqslant 19)$ of independent reflections were measured by the use of $\omega-2\theta$ scan (scan range, $3° \leqslant 2\theta < 150°$), 1815 taken as observed N_o with $I \geqslant 3\sigma(I)$, 1790 unobserved reflections, corrected for Lorentz and polarization effects. Three standard reflections (503, 336 and 067) were measured every hour, but no intensity variation was detected. The crystal data are listed in Table 1.

The structure was solved by direct methods (MULTAN) [11]. Full-matrix least-squares $\Sigma\bar{w}(\Delta F)^2$ minimized, 334 parameters refined N_V with all non-hydrogen atoms

TABLE 1. Crystal data

Formula	$C_{28}H_{29}Cu_2N_3O_4$
Molecular weight	598.64
System	Monoclinic
Space group	$P2_1/n$
a (Å)	9.890(3)
b (Å)	17.645(3)
c (Å)	15.414(5)
β (°)	90.96(3)
V (Å^3)	2690(2)
Z	4
D_c (g cm^{-3})	1.48
μ (cm^{-1})	22.2 (Cu Kα; $\lambda = 1.54184$ Å)

TABLE 2. Atomic coordinates for the non-hydrogen atoms

Atom	x	y	z	B_{eq} (Å^2)
Cu(1)	0.2778(2)	0.21680(9)	0.3798(1)	4.99(8)
Cu(2)	0.2522(2)	0.02885(9)	1.1120(1)	5.14(9)
O(1)	0.299(1)	0.1416(4)	0.4711(5)	7.3(5)
O(2)	0.236(1)	0.2274(5)	0.5553(6)	11.6(6)
C(3)	0.273(1)	0.1647(6)	0.5454(7)	5.2(6)
C(4)	0.288(1)	0.1103(7)	0.6190(8)	7.2(8)
C(5)	0.288(1)	0.1438(7)	0.7080(8)	7.8(9)
C(6)	0.295(1)	0.0916(7)	0.7801(8)	7.8(8)
C(7)	0.278(1)	0.1252(7)	0.8645(8)	6.3(7)
C(8)	0.278(1)	0.0695(7)	0.9437(7)	5.8(6)
O(9)	0.253(1)	0.0992(4)	1.0150(5)	6.9(4)
O(10)	0.285(1)	0.0011(5)	0.9293(5)	10.4(6)
C(11)	0.399(1)	0.3089(6)	0.3950(8)	5.5(6)
C(12)	0.341(1)	0.3082(6)	0.3116(6)	4.6(5)
C(13)	0.239(1)	0.3739(5)	0.3122(5)	3.8(4)
C(14)	0.326(1)	0.4444(6)	0.3130(7)	4.9(6)
C(15)	0.387(1)	0.4448(6)	0.3979(8)	5.7(6)
C(16)	0.336(1)	0.3740(6)	0.4439(8)	5.7(6)
C(17)	0.191(1)	0.3709(6)	0.4090(7)	4.7(5)
N(21)	0.1316(9)	0.1692(4)	0.3090(5)	4.3(1)
C(22)	0.046(1)	0.1195(7)	0.3441(7)	5.6(6)
C(23)	−0.058(1)	0.0866(8)	0.2999(9)	7.4(8)
C(24)	−0.071(1)	0.1002(7)	0.216(1)	7.8(8)
C(25)	0.015(1)	0.1508(7)	0.1711(8)	6.9(8)
C(26)	0.113(1)	0.1808(7)	0.2225(7)	6.2(7)
N(31)	0.4026(9)	0.0754(5)	1.1833(5)	4.8(4)
C(32)	0.490(1)	0.1228(6)	1.1451(8)	6.0(6)
C(33)	0.590(1)	0.1590(7)	1.1924(8)	6.2(7)
C(34)	0.604(1)	0.1507(6)	1.2800(8)	6.5(7)
C(35)	0.510(1)	0.1019(7)	1.3172(9)	7.6(8)
C(36)	0.411(1)	0.0670(7)	1.2707(8)	5.6(6)
N(41)	0.266(1)	0.2928(7)	0.0425(7)	9.8(8)
C(42)	0.386(1)	0.3313(9)	0.0507(9)	9.2(9)
C(43)	0.396(1)	0.4083(8)	0.061(1)	9.(9)
C(44)	0.279(1)	0.4458(7)	0.0517(8)	8.5(8)
C(45)	0.159(1)	0.4137(8)	0.042(1)	9.4(9)
C(46)	0.157(1)	0.3399(9)	0.039(1)	9(1)

B_{eq} is defined as $\frac{4}{3}$Tr $(B \times G)$ where B is the thermal motion tensor and G is the direct metric tensor.

TABLE 3. Relevant bond lengths with their estimated standard deviations

Cu(1)–O(1)	1.943(8)	C(6)–C(7)	1.442(18)
Cu(1)–C(12)	2.031(12)	C(7)–C(8)	1.567(17)
Cu(1)–N(21)	1.984(9)	C(8)–O(9)	1.245(14)
Cu(1)–C(11)	2.032(12)	C(8)–O(10)	1.229(15)
Cu(2)–O(9)	1.944(8)	C(11)–C(12)	1.399(17)
Cu(2)–N(31)	2.009(9)	C(11)–C(16)	1.515(17)
Cu(2)–C(14)	2.046(12)	C(12)–C(13)	1.537(16)
Cu(2)–C(15)	2.027(12)	C(13)–C(14)	1.511(16)
O(1)–C(3)	1.247(14)	C(13)–C(17)	1.574(15)
O(2)–C(3)	1.179(16)	C(14)–C(15)	1.431(17)
C(3)–C(4)	1.491(17)	C(15)–C(16)	1.527(17)
C(4)–C(5)	1.494(19)	C(16)–C(17)	1.523(19)
C(5)–C(6)	1.445(19)		

TABLE 4. Relevant bond angles with their estimated standard deviations

O(1)–Cu(1)–C(11)	113.9(8)	C(4)–C(5)–C(6)	116.9(22)
O(1)–Cu(2)–C(12)	152.4(8)	C(5)–C(6)–C(7)	115.3(22)
O(1)–Cu(1)–N(21)	100.4(7)	C(6)–C(7)–C(8)	116.6(20)
C(11)–C(1)–C(12)	40.3(8)	C(7)–C(8)–O(9)	115.2(19)
C(11)–Cu(1)–N(21)	145.7(8)	C(7)–C(8)–O(10)	118.3(20)
C(12)–Cu(1)–N(21)	106.3(7)	O(9)–C(8)–O(10)	125.9(21)
O(9)–Cu(2)–N(31)	98.5(7)	C(2)–O(9)–C(8)	114.4(14)
O(9)–Cu(2)–C(14)	154.9(5)	C(12)–C(11)–C(16)	107.3(18)
O(9)–Cu(2)–C(15)	114.8(5)	C(11)–C(12)–C(13)	104.3(17)
N(31)–Cu(2)–C(14)	105.8(5)	C(12)–C(13)–C(14)	104.3(15)
N(31)–Cu(2)–C(15)	146.7(5)	C(12)–C(13)–C(17)	100.9(15)
C(14)–Cu(2)–C(15)	41.1(12)	C(14)–C(13)–C(17)	101.6(15)
C(1)–O(1)–C(3)	114.8(14)	C(13)–C(14)–C(15)	104.0(17)
O(1)–C(3)–O(2)	119.8(21)	C(14)–C(15)–C(16)	106.5(18)
O(1)–C(3)–C(4)	118.0(20)	C(11)–C(16)–C(15)	104.3(18)
O(2)–C(3)–C(4)	122.2(21)	C(11)–C(16)–C(17)	101.0(17)
C(3)–C(4)–C(5)	116.3(21)	C(15)–C(16)–C(17)	100.4(17)
		C(13)–C(17)–C(16)	92.1(15)

anisotropic. At the end of isotropic refinement an empirical absorption correction [12] was applied; the relative transmission coefficients ranged from 0.779 to 1.684 (mean value, 1.005). The positions of H atoms were generated from assumed geometries and included in the structure factor calculations, but they were not refined. The final $R = 0.080$, $R_{\overline{\omega}} = 0.102$, $R_{tot} = 0.158$, $S = [\Sigma\omega(\mid F_o \mid - \mid F_c \mid)^2/N_o - N_v]^{1/2} = 3.43$, $\omega = 4F_o^2/\sigma^2(F_o^2)$ and $(\Delta/\sigma)_{max} = 0.21$. The highest peak in the final difference map was 0.7(1) electron Å^{-3}. All calculations were performed on a PDP 11/34 minicomputer; the programs and sources of scattering factors are given in ref. 13. The atomic coordinates for non-hydrogen atoms are listed in Table 2. The relevant bond distances and angles are given in Table 3 and 4. Tables of hydrogen atom coordinates and thermal parameters, and a complete list of bond lengths and angles have been diposited with the Cambridge Crystallographic Data Centre.

Results and discussion

The ability of the dinuclear copper(I) adipinate pyridine complex to form stable olefin and diolefin complexes was examined. The copper(I) adipinate complex prepared in situ from adipinatobis(pyridine)copper(II) by the use of metallic copper in pyridine did not give isolable olefin complexes with ethylene, propylene, hexene-1, cyclohexene, diethyl maleate or diethyl fumarate or with the cyclic polyolefins cyclooctadiene, cycloheptatriene and dicyclopentadiene were unsuccessful. However when NBD was added to the pyridine solution of copper(I) adipinate, colourless prisms separated immediately from the solution. The complex can-

not be dried in vacuum because of the loss of coordinated and lattice pyridine. The IR spectrum does not differ significantly from that of the starting complex. The stretching frequency of the double bond in NBD at 1550 cm^{-1} [14] is shifted to a lower wavenumber, but it could not be found, probably because of the overlap with the broad $\nu(CO_2)$ bands at 1560 and 1405 cm^{-1}. The NBD copper complex is extremely air and moisture sensitive and, it was not possible to record ^1H and ^{13}C nuclear magnetic resonance spectra. Line broadening for copper complexes as a result of paramagnetic impurities is a very common phenomenon.

The X-ray structure determination of the copper(I) adipinate NBD complex (as a pyridine solvate) is depicted in Fig. 1. This shows that the compound has a zigzag polymeric structure. The carboxylate groups of the adipinate moiety coordinate to each copper(I) in a monodentate fashion. This is consistent with the value of $\nu(CO_2)_{as} - \nu(CO_2)_s$ of 155 cm^{-1} [15].

The asymmetric unit consists only of the numbered part of the plot, which contains two copper(I) atoms, two pyridine ligands, the bridging adipinate and NBD chelates and a pyridine inclusion. Both copper atoms have the same environment, consisting of the nitrogen atom of the pyridine, an oxygen atom of the adipinate ligand and the olefin are in trigonal planar arrangement. The molecules are linked by alternating adipinate and norbornadiene chelates to give a polymeric structure, which has a crystallographic twofold screw axis (2_1) along the b direction. The adjacent n diagonal glide related chains are well separated. Relevant bond distances and angles in both coordination spheres agree within experimental error. The geometries of the ligands are normal. The shortest intermolecular distances
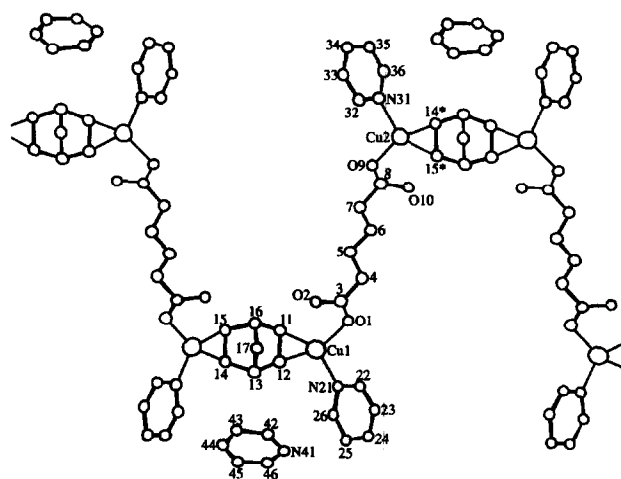

Fig. 1. A perspective view of the complex with atomic labelling. The bare numbers are for carbon atoms unless indicated otherwise. H atoms are not shown.
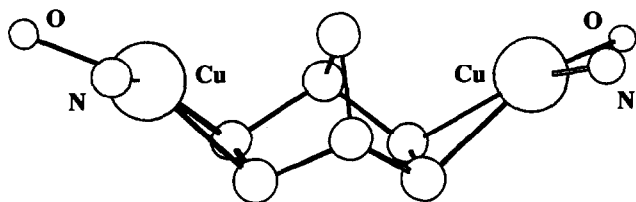
Fig. 2. A perspective view of the coordinated NBD.

between copper atoms and the pyridine molecules of solvation are as follows: Cu(1)–C(46), 4.55(1) Å; Cu(2)–N(41), 4.78 Å.

Both copper(I) ions are coordinated *exo* to the double bonds in NBD (Fig. 2). The copper–oxygen bond distances (Cu(1)–O(1), 1.943(8) Å; Cu(2)–O(9), 1.944(8) Å) are somewhat shorter then these in bidentate carboxylato copper complexes (C–O$_{av}$, 1.98 Å) [15]. The copper–nitrogen bond distances (Cu(1)–N(21), 1.984(9) Å; Cu(2)–N(31), 2.009(9) Å) are shorter than those in [Cu$_2$(PhCO$_2$)$_4$(py)$_2$] (2.170(3) Å) [16]. The C=C double bonds of the copper-coordinated NBD (C(11)–C(12), 1.399(17) Å; C(14)–C(15), 1.431(17) Å) are much longer than that in [CuCl(NBD)]$_4$ (1.345(11) Å), and the uncoordinated olefinic C=C bond is even shorter (1.317(11) Å) [5]. The coordinated double bonds in NBD · 2AgNO$_3$ have C=C bond distances of 1.39(5) Å [17]. The copper–carbon bond lengths which average value 2.034 Å, are much shorter than the metal–carbon bonds in the silver complex (Ag–C$_{av}$, 2.36 Å). In the [CuCl(NBD)]$_4$ complex bond lengths are much the same (2.051 and 2.111 Å) as found here [5]. The relatively similar Cu–C bond lengths found here are probably due to the high symmetry of the molecule and the absence of ligands with high steric demands.

Acknowledgement

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