© *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 62, 4092—4094 (1989)* [Vol. 62, No. 12

A New Crystalline Form of Bis(1,2-diphenyl-1,2-ethenedithiolato)nickel: Asymmetric β-Ni(dpedt)$_2$

Michel MEGNAMISI-BELOMBE* and Bernhard NUBER†
Department of Inorganic Chemistry, Faculty of Science, P.O. Box 812,
The University of Yaoundé, Yaoundé, Cameroon
†Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270,
D-6900 Heidelberg 1, West Germany

(Received March 24, 1989)

Synopsis. The full structure of a new crystalline form of bis(1,2-diphenyl-1,2-ethenedithiolato)nickel, β-Ni(dpedt)$_2$, has been determined by single crystal X-ray diffraction at room temperature. The structure was refined by full matrix least-squares to a final R_w=0.038. Comparison of this triclinic ($P\bar{1}$) structure with the monoclinic ($P2_1/n$) α-form established previously reveals that the difference between the two structures is basically due to a different conformation of the phenyl rings, which gives rise to *dissymmetry* in β-Ni(dpedt)$_2$.

Since the discovery of Ni(dpedt)$_2$,[1] bis-dithiolato complexes of transition metals have attracted a great deal of scientific interest in inorganic chemistry. Synthetic and experimental findings[2] as well as structural systematics[3,4] of these materials have been reviewed, and an extensive theoretical treatment has been presented.[5] We recently introduced a new concept[6] for preparing a wide range of stacking solids made up of alternated square planar sulfur (S)-containing, and square planar nitrogen (N)-containing complexes. In an attempt to fabricate solids of this type, we have employed, on the one hand, α-Ni(dpedt)$_2$[3] as the S-containing component and, on the other hand, either bis(1,2-diphenylethanedione dioximato)cobalt(II), Co(dpg)$_2$, or bis(butanedione dioximato)copper(II), Cu(dmg)$_2$, as the N-containing components. Although we failed to produce the desirable stacking materials with so-called pseudo-(SN)$_x$ bundle-structure,[6] we interestingly obtained, in both cases, the novel asymmetric β-Ni(dpedt)$_2$, which may be regarded as a potentially versatile optically active solid system. We therefore have determined its full structure and have compared it with the previously known α-modification,[3] as we report in the following.

Experimental

Material Preparation. Single crystals of β-Ni(dpedt)$_2$ were obtained in two different preparations. In a first preparation, analytical grade Co(dpg)$_2$ (100 mg) was dissolved in a mixture of warm methyl cyanide and chloroform (50 ml+50 ml) and filtered (brown solution). Analytical grade α-Ni(dpedt)$_2$[1,3] (100 mg) was dissolved similarly and filtered (blue-green solution). The two solutions were mixed together and refluxed for 15—20 min. The mixture was filtered warm, and the dark-green filtrate was left to concentrate by slow evaporation at ca. 40 °C. When the solvent volume was reduced to 150 ml, shiny long crystals appeared. They grew larger as concentration of the solution progressed until the volume was reduced to about 50 ml. The long black crystals were separated by filtration, washed with some 100 ml of high purity diethyl ether (sparingly soluble with green color). The yield was 70 mg of slightly dichroic prisms. The density determined by flotation in a mixture of dibromomethane and 1,3,5-trimethylbenzene was D_m=1.44 Mg m^{-3}. The second preparation was carried out in a closely similar manner by using analytical grade Cu(dmg)$_2$ (30 mg) dissolved in warm chloroform (40 ml), and α-Ni(dpedt)$_2$ (55 mg) dissolved in chloroform (40 ml).

Table 1. Experimental and Computational Details

Crystal shape	Prismatic
Crystal size /mm^3	0.2×0.3×0.3
Possible indep. reflections	3878
Reflections observed $I>2.5\sigma(I)$	3256
Reflections for ψ-scans	6
2θ range /°	3—60
Min. transmission (max.=1)	0.90
μ(Mo $K\alpha$)/mm^{-1}	1.094
R_{int} (from merging)	0.014
parameters for least-squares	250
R_w, R	0.038, 0.044
Goodness-of-fit	2.59
Max. shift/error	0.07
Extremes in diff. Fourier/e Å^{-3}	+0.28, −0.32

Structure Determination. A suitable crystal from each batch was analyzed independently by X-ray diffraction at room temperature. Crystal data were collected on a Siemens-Stoe AED 2, or on a Syntex R3, four-circle automatic diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ=0.7107 Å).

Crystal Data. Virtually identical data were obtained for both batches of crystals. $C_{28}H_{20}NiS_4$, M_r=543.4, triclinic, space group $P\bar{1}$, a=10.135 (2) Å, b=10.212 (1) Å, c=12.631 (1) Å; α=79.53 (3)°, β=89.08 (3)°, γ=82.02 (3)°; V=1273.02 Å^3; Z=2; D_c=1.42 Mg m^{-3}, D_m=1.44 Mg m^{-3}.

Table 1 summarises further experimental and computational details. The structure was solved by the Patterson methods and completed by Fourier syntheses. It was refined by full matrix least-squares, based on F with weight $w=\sigma(|F|)^{-2}$. The phenyl rings were refined as rigid groups. The calculations were carried out on an Eclipse S140 computer with SHELXTL program[7] which uses scattering factors from "International Tables",[8] and takes anomalous dispersion into account.[9] The final refinement with anisotropic thermal parameters for non-hydrogen atoms, and isotropic parameters for hydrogen atoms yielded R (R_w)=0.044 (0.038). An empirical absorption correction (μ(Mo $K\alpha$)=1.094 mm^{-1}) was applied using ψ-scans of 6 reflections (8<2θ<43°).

Results and Discussion

The purpose of this note is to highlight the structural divergence that exists between the two phases of the same chemical compound, Ni(dpedt)$_2$. Final atomic coordinates with their equivalent isotropic thermal parameters for the β-phase elucidated here are listed in Table 2. Figure 1 displays a molecular view of this phase with atom labeling scheme. For both crystalline forms, such a molecular entity consists of two specific structural cores, namely, the chelate plane NiS$_4$C$_4$ (comprising the four non-benzenic C atoms), and the four phenyl rings. Comparison of these molecular spheres between the two modifications reveals rather nicely matching values in terms of corresponding bond distances and angles. For the β-phase, the following bond lengths are observed: Ni-S 2.120—2.127 (1) Å; C=C 1.404—1.424 (6) Å; S-C 1.695—1.701 (4) Å; C-C$_{Ph}$ 1.474—1.488 (5) Å; average (C-C)$_{Ph}$ 1.395 (0) Å; the following angles are measured: S1-Ni-S3 91.1 (1)° S1-Ni-S4 88.0 (1)° S2-Ni-S4 91.3 (1)° S2-Ni-S3 89.5 (1)° C-S-Ni 105.9—106.1 (2)° S-C=C 117.9—118.9 (3)°.

Angles between selected planes for the β-phase are listed in Table 3. By comparison with the previously established α-phase,[3] it is seen that the basic difference between the two structural modifications arises as a result of different conformations of the phenyl groups.

Table 2. Final Atomic Coordinates (×10^5) and Their Equivalent Isotropic Thermal Parameters (×10^4)[a]

Atom	X	Y	Z	B_{eq}/Å^2
Ni1	6135(6)	26386(6)	4182(5)	511(2)
S1	25928(12)	16483(13)	6853(9)	542(5)
S2	−14242(11)	34844(12)	1951(9)	498(4)
S3	6301(11)	33241(12)	19081(9)	526(5)
S4	6170(12)	19169(13)	−10571(10)	596(5)
C1	−9612(42)	23588(41)	−15623(33)	457(16)
C2	−19242(40)	30523(38)	−9529(31)	417(15)
C3	21621(41)	26797(41)	24840(32)	430(16)
C4	30556(39)	18903(40)	19163(31)	417(15)
C11	24233(25)	30379(28)	35408(23)	449(16)
C12	36785(25)	33287(28)	37782(23)	530(10)
C13	39138(25)	36833(28)	47671(23)	668(22)
C14	28938(25)	37471(28)	55186(23)	740(24)
C15	16386(25)	34563(28)	52812(23)	702(23)
C16	14033(25)	31017(28)	42923(23)	544(10)
C21	44014(29)	12078(25)	22985(17)	426(16)
C22	54953(29)	13936(25)	16311(17)	523(10)
C23	67630(29)	7570(25)	19756(17)	606(20)
C24	69368(29)	−654(25)	29875(17)	596(20)
C25	58429(29)	−2512(25)	36549(17)	543(10)
C26	45752(29)	3855(25)	33104(17)	482(17)
C31	−12209(27)	20170(21)	−26176(23)	451(16)
C32	−18589(27)	29939(21)	−34345(23)	522(17)
C33	−20654(27)	26775(21)	−44424(23)	630(21)
C34	−16340(27)	13841(21)	−46335(23)	656(22)
C35	−9960(27)	4072(21)	−38167(23)	604(21)
C36	−7895(27)	7237(21)	−28087(23)	511(18)
C41	−33628(26)	33423(23)	−12302(20)	411(15)
C42	−40508(27)	46144(23)	−11923(20)	443(16)
C43	−54195(26)	48791(23)	−13963(20)	510(10)
C44	−61004(26)	38716(23)	−16381(20)	603(20)
C45	−54125(26)	25995(23)	−16760(20)	586(20)
C46	−40437(26)	23349(23)	−14721(20)	530(10)

a) Equivalent isotropic B_{eq} defined as one-third of the trace of the orthogonalized B_{ij} tensor. Last significant esd digits for each term are given in parentheses.

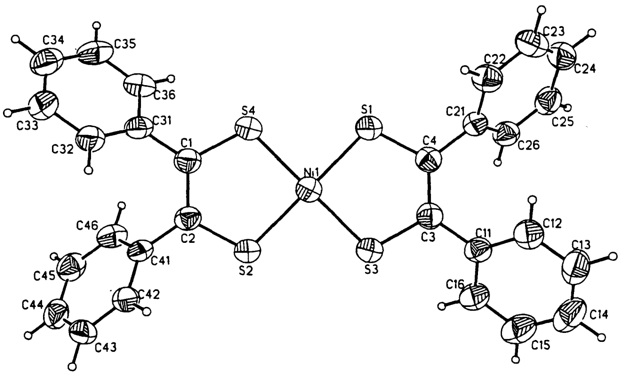

Fig. 1. A molecule of β-Ni(dpedt)$_2$ with atom labeling, seen onto the Ni,S1-S4,C1-C4 plane.

In the α-phase, the conformation allows for the molecule to possess a $\bar{1}$ symmetry; in the β-phase, by contrast, the conformation is such that the molecule totally lacks reflection symmetry, as clearly revealed by Table 3. Thus, β-Ni(dpedt)$_2$ is a *disymmetric* molecule, and is expected to exhibit optical activity. This finding obviously adds a new dimension to the scientific and technological relevance of this chemical compound, which now may be viewed as a potentially versatile chiroptical system in its β-phase.

One may reasonably assume that the stabilization of the phenyl librational energy into this dissymmetric conformation is influenced, during material preparation, by the presence of the Co(dpg)$_2$ or Cu(dmg)$_2$ complexes. It seems rather hard to say, however, *why* and *how* this influence could actually be brought about!

Michel Mégnamisi-Bélombé wishes to thank "Stiftung Volkswagenwerk" (West Germany) for partial support of this work via its "Partnership Program".

We thank Dr. H. Pritzkow, Heidelberg, for his help with a set of diffraction data.

References

1) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

2) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1963).

3) D. Sartain and Mary R. Truter, *J. Chem. Soc. A*, **1967**, 1264.

4) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).

5) S. Alvarez, R. Vincente, and R. Hoffmann, *J. Am. Chem. Soc.*, **107**, 6253 (1985).

6) a) M. Mégnamisi-Bélombé, *J. Phys. (Paris), Colloq.*, **44**, C3-717 (1983). b) M. Mégnamisi-Bélombé, *Synth. Met.*,

Table 3. Angles (°) between Selected Planes (e.s.d.'s of Planes: −0.1043—+0.0902)

Plane	Defined by	Angles to planes 1	2	3	4	5
1	Ni1,S1-S4,C1-C4					
2	C11-C16	34.0				
3	C21-C26	52.7	53.5			
4	C31-C36	45.5	79.5	71.1		
5	C41-C46	51.0	62.8	103.6	59.6	

18, 605 (1987).

7) G. M. Sheldrick, SHELXTL. An integrated system for solving, refining and displaying crystal structures from diffraction data, University of Göttingen, FRG (1983). (Revision 5.1, Eclipse 32K Version, 1985).

8) International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974). Present distributor: D. Reidel, Dordrecht, The Netherlands.

9) Observed and calculated structure factors (20 pages), atomic parameters of hydrogen atoms and anisotropic thermal parameters have been deposited as Document No. 8898 at the Office of the Editor of Bull. Chem. Soc. Jpn.