Crystal structure of new Ni(II) complex with non-symmetrical bis-enaminone from powder diffraction data

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Received December 18, 1998; accepted July 5, 1999

Abstract. The crystal structure of $C_{22}H_{32}BrN_2NiO_2$ was *ab initio* solved from conventional X-ray powder data by combination of few powder diffraction techniques. After the intensity estimating procedure based on texture method, the orientation and approximate position of the molecule was found by the Patterson methods. Next, Patterson and direct method search program PATSEE was used to locate the molecule more precisely. Missing atoms of flexible groups and final refinement was performed by Rietveld method. The structure consists of flat molecules connected by van der Waals forces. The compound crystallises in the monoclinic space group $P2_1/c$ (No. 14) with $a = 10.362(3)$ Å, $b = 18.468(3)$ Å, $c = 12.066(3)$ Å, $\beta = 124.53(1)°$, $Z = 4$, and contains 28 atoms in asymmetric unit.

Introduction

The main obstacle to structure solution from powder diffraction data is the problem of overlapping reflections. Despite many theoretical achievements in this field [1–8], the most complicated structures from powder data have been solved by *conventional methods* [9–11], neglecting all overlapping reflections. However, such an approach seems to be very unattractive and time consuming, particularly in the case of laboratory data. Since only a limited number of reflections has been used, structure models based on these data, in general, contain only a small part of the structure. Difference Fourier maps calculated subsequently (even using Rietveld method for F_o estimation) are flat, thus not easy for interpretation. It makes the complete structure solution in the case of a small number of heavy atoms very difficult and sometimes even impossible.

Recently we have started a structural investigation of polycrystalline samples using the texture as an intensity-separating device [12] to increase the number of 'single crystal like intensities'. In this paper we present the results of 'a simplified texture-based method' in *ab initio* structure solution of unknown compound. We report the crystal structure solution of a complex metallorganic compound, a structure with 28 atoms in the asymmetric unit. Intensity estimating procedure based on texture separating routine allowed location of heavy atoms. Next, the Patterson search program PATSEE [13] using intensities separated by texture method was successfully used to locate the molecule more precisely. In our work we use X-ray data collected by a conventional powder diffractometer (Philips X'Pert) as well as patterns obtained from Guinier cameras.

Data collection and space group determination

For structure determination studies, 3 diffraction patterns were used; one Guinier picture and two patterns obtained from powder diffractometer. Patterns with the *low* and *high* texture were selected from a few patterns recorded for the sample. Details of the data collection are presented in Table 1. The positions of the reflections were determined using PEAK program by Sonneveld & Visser [14]. The powder diffraction pattern of the investigated compound was indexed in the monoclinic system using indexing program written by Visser [15]. From the analysis of the systematic extinction the space group was found to be $P2_1/c$.

Intensity estimation and structure solution

In the beginning of the studies we analysed the Guinier data only. For the structure solution a part of the diffraction pattern (up 50° 2θ) was used. The diffraction pattern was decomposed for single and overlapping intensities by LSQPROF [16] program, with an R value 0.56%. In a 0.5 FWHM as separation limit 89 single reflections were found, while the total number of reflections possible in this range was 329. The single reflections were used by SHELXS-86 and in the resulting Patterson map a few strong peaks were found. Assuming that one strong peak is Br and the other is Ni we have built a few heavy atom models as an input for Rietveld calculations. Unfortunately, the attempts of completing the molecule by stan-

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Table 1. Details of data collection and structure refinement for $C_{22}H_{32}BrN_2NiO_2$.

Measurement^a	Guinier-Lené camera	PW3710 X'PERT
Radiation	Cu$K_{\alpha 1}$, SiO_2 monochromator	CuK_α
2θ range	4.5–70	7–70
Step scan increment,	0.01	0.02
Count time [sec/step]		16
Standard peak: hkl, 2θ	$12\bar{1}$, 13.19	
R for standard peak [%]	2.7%	
Space group	$P2_1/c$ (No. 14)	
a [Å]	10.362(3)	
b [Å]	18.468(8)	
c [Å]	12.066(3)	
β [°]	124.53(1)	
V [Å^3]	1902.23(4)	
Number of observations	5816	2717
Number of reflections	659	666
Number of atoms	28	
Number of structural parameters refined	85	
Number of profile parameters refined	10	
R_F	10.7	10.6
R_I	17.1	17.6
R_{wp}	23.3	24.8
Max. shift/error	0.05	
Preferred orientation vector & factor		$[10\bar{1}]$, −0.38(3) $[10\bar{1}]$, −0.18(3)

a: parameters listed if not equal

dard procedures failed, so we decided to complete the model by other methods. First of all we decided to increase the number of initial intensities (to locate the bigger part of the molecule) using a method described recently by us [12]. The basic idea of this method is as follows: for the same compound but with different texture, different diffraction patterns should be obtained. Next, using these patterns we have been able to find a set of the most appropriate intensities (including overlapping ones) corresponding to all observed patterns. In this study we analysed patterns with different texture collected by powder diffractometer. The most probable texture direction (found as 10-1) and texture coefficients (G in formula $\exp(G \cos 2\alpha)$) were evaluated using described methods [12]. These data were used for intensity separation. Using the most suitable pairs of closely overlapping peaks (not affected by high background or high noise), intensities of 34 overlapping peaks were determined. New intensity data (89 single + 34 overlapping lines) were used in calculations carried out by SHELXS-86 program. In this case the position of heavy atoms could be very easily found by the program. Since the molecule is very long and big, Patterson and Direct Methods search program PATSEE was used to locate whole more precisely. In this way we avoided very time consuming Rietveld refinement, and ambiguities in initial stages of Rietveld refinement and Fourier maps analysis. Having one benzene ring which can rotate, PATSEE program had to consider a model with one torsion angle of freedom. In our study this angle changed from 0 to 180° with 10° increments. For each torsion angle a suitable number (between 20000–40000) of random orientations of the whole molecule was generated. For each orientation an agreement between Patterson map and interatomic distances was calculated. For the 5 best orientations, translational test were performed, suitable number of random translations was generated and for each translation special figure of merits were calculated. Solutions with too short distances were automatically rejected. Next,

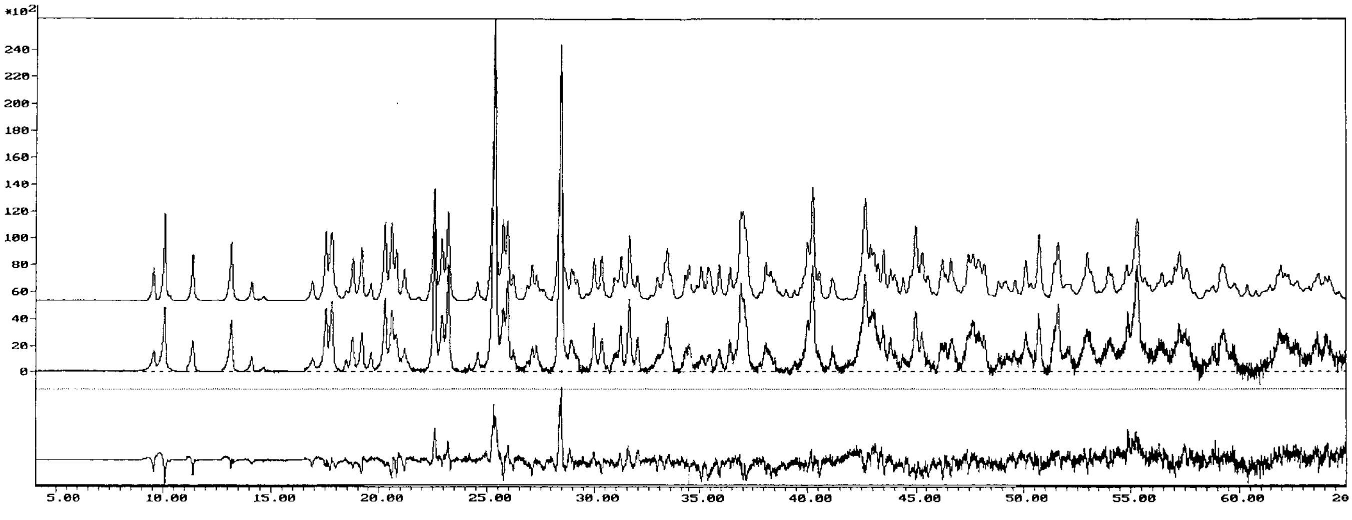

Fig. 1. Calculated, observed and difference Rietveld plots.

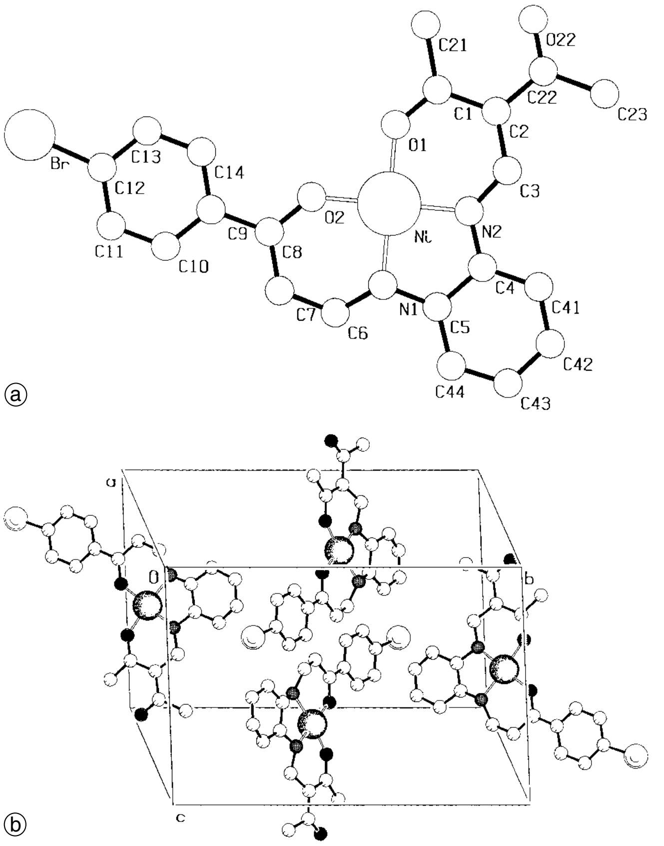

Fig. 2. The $C_{22}H_{32}BrN_2NiO_2$ molecule with numbering scheme **(a)** and projection of the structure **(b)**.

Table 2. List of atomic parameters.[a]
The e.s.d. of the last significant digit is given in parentheses.

atom	*x*	*y*	*z*
Ni	1.304(3)	−0.025(1)	0.555(3)
Br	0.803(3)	0.281(1)	0.717(2)
N1	1.378(7)	−0.085(3)	0.714(5)
O1	1.21(1)	0.023(5)	0.390(7)
N2	1.413(9)	−0.084(3)	0.506(5)
O2	1.207(9)	0.036(4)	0.606(5)
C1	1.21(1)	0.018(5)	0.286(7)
C21	1.10(2)	0.063(6)	0.16(1)
C2	1.306(8)	−0.041(3)	0.279(5)
C22	1.311(9)	−0.047(4)	0.160(6)
022	1.23(1)	−0.004(5)	0.065(7)
C23	1.40(2)	−0.111(7)	0.15(1)
C3	1.37(1)	−0.098(3)	0.378(6)
C4	1.490(9)	−0.137(4)	0.604(7)
C41	1.57(1)	−0.194(5)	0.591(9)
C42	1.68(1)	−0.233(5)	0.71(1)
C43	1.67(1)	−0.232(5)	0.82(1)
C44	1.59(1)	−0.178(6)	0.831(7)
C5	1.50(1)	−0.128(4)	0.725(8)
C6	1.403(9)	−0.052(2)	0.828(5)
C7	1.28(1)	−0.008(5)	0.818(7)
C8	1.197(9)	0.040(4)	0.709(5)
C9	1.091(7)	0.093(3)	0.708(6)
C10	1.09(1)	0.102(4)	0.821(8)
C11	1.01(1)	0.159(5)	0.829(8)
C12	0.919(4)	0.203(4)	0.718(8)
C13	0.93(1)	0.197(4)	0.608(9)
C14	1.00(1)	0.139(6)	0.600(7)

a: *U* (overall temperature factor) 0.07637

the best solutions we tested by the Rietveld method. It was found that the solution with the lowest R_E value (~35%) was the true one. The missing atoms were found from difference Fourier map.

Structure refinement

The structure was completed and further refined by Rietveld method using the PC version of XRS-82 [18]. Initially only a part of the pattern (from 4° to 50° 2θ) was used. Peak range was limited to 3 FWHM. First, Ni and Br were refined, then stepwise further atoms were refined. After refinement of all atoms by the difference Fourier methods, two atoms: C23 and O22 bonded to C22 atom (see Fig. 2) were found, decision which one is O or C atom was based on the bond distances. As independent observations, constraints for interatomic distances and angles were introduced to the refinement procedure; in total 64 distances and angles were used as constraints, their total weight was however, about 30% of that assigned to diffraction data in the final refinement cycles. For the final refinement the whole pattern up to 74° 2θ was used and peak range was set to 5 FWHM.

Table 3. List of bond distances (Å).

atom 1	atom 2	bond e.s.d.	atom 1	atom 2	bond e.s.d.
Ni	N1	1.95(7)	N1	C5	1.41(13)
	N2	1.89(9)		C6	1.39(10)
	O1	1.87(8)			
	O2	1.84(10)	N2	C3	1.37(10)
				C4	1.39(9)
O1	C1	1.29(15)	O2	C8	1.30(12)
C1	C2	1.48(13)	C21	C1	1.55(12)
C2	C22	1.47(12)	C22	C23	1.55(17)
	C3	1.45(8)		022	1.24(10)
C4	C5	1.43(14)	C5	C44	1.42(11)
	C41	1.41(15)			
C41	C42	1.38(13)	C42	C43	1.37(21)
C43	C44	1.40(17)	C6	C7	1.44(15)
C7	C8	1.42(9)	C8	C9	1.47(11)
C9	C10	1.38(15)	C10	C11	1.38(15)
C11	C12	1.38(10)	C12	C13	1.38(17)
C13	C14	1.38(17)	C14	C9	1.37(10)
Br	C12	1.87(7)			

What is important: all bond distances were restrained, C—C distances in the aromatic rings were set to 1.39 Å, and 1.45 Å for all other C—C bonds. Each distance and angle have had the same weight in the refinement.

The observed, calculated as well as difference patterns are presented in Fig. 1. Atomic positions, results of the final Rietveld refinement are presented in Table 3. The molecule with numbering scheme and projection of the structure is shown in Fig. 2a and 2b.

Structure description

The final atomic parameters and most important interatomic distances in the molecule are listed in Tables 2 and 3. The precision of the atomic positions is rather low, large e.s.d.'s are not surprising in the case of such a complicated structure which was refined using laboratory data. Moreover, the e.s.d. of atomic positions and bond distances were calculated according to Scott [19] and as such, they are a few times higher than those obtained from other Rietveld programs.

The structure consists of almost flat molecules, the angles between the central part of the molecule (atoms O1, O2, N1, N2) and phenyl rings (C9, C10, C11, C12, C13, C14 and C4, C41, C42, C43, C44, C5) are 7.2 and 9.3°. From the molecular packing it is observed that no intermolecular contacts in this structure are less than the sum of the corresponding van der Waals radii. This suggests that there are no forces other than van der Waals forces stabilising the structure.

Concluding remarks

The main achievements of our investigations can be listed as follows:

- Applied methods allow the structure solution of a 28-atom structure to be achieved from laboratory powder data.
- Diffraction patterns with different texture were used in active way in the process of *ab initio* structure solution.

Chemical synthesis

The aim of the synthesis was Ni(II) complex **4** containing tetradentate ligand having only single reactive acetyl group. This ligand may be used to the investigation of the influence of the noncoordinated carbonyl group on the cyclization process.

The non-symmetrical Schiff bases ligands were most commonly synthesised from the monocondensation products ("half units") of several diamines with 1,3-diketones [20–22] and orthosubstituted aromatic carbonyl compounds [23–29] (see scheme below).

The starting 3-ethoxyvinylidene-2,4-pentanedione **2** was prepared by the literature method [30]. The 3-[N-(2′-aminophenyl)amino]-1-(4′-bromophenyl)-2-propen-1-one **1** was prepared from reaction p-bromobenzoylacetaldehyde and 1,2-diaminobenzene [31].

Preparation of 3-acetyl-(6,7)-benzo-11-(4′-bromophenyl)-5,8-diazaundodeca-3,9-diene-2,11-dione 3

To the hot solution of **1** (1.7 g, 0.008 mole) in ethanol (50 cm^3) a solution of **2** (1.26 g, 0.008 mole) in ethanol (10 cm^3) was added. The mixture was refluxed for 2 h, then cooled. The yellow precipitate was collected by filtration and was recrystallized from ethanol. Yield 1.6 g (47%)
m.p.: 456–457 K
elemental analysis: $C_{21}H_{19}BrN_2O_3$
calc.: C 59.03 H 4.48 N 6.56
found.: C 59.12 H 4.35 N 6.58

^{1}H NMR chloroform d$_1$: $\delta = 2.36$ (s, 3 H, i-H), 2.59 (s, 3 H, k-H), 6.09 (d, J = 7.9 Hz, H; b-H); 7.14–7.30 (m, 4 H, 6/7/8/9-H), 7.46 (dd, J = 11.5 Hz, J = 8.0 Hz, 1 H; c-H), 7.57 (d, J = 8.0 Hz, 2 H; 3-H), 7.81 (d, J = 8.0 Hz, 2 H; 2-H), 8.14 (d, J = 12.1 Hz, 1 H; f-H), 12.27 (d, J = 11.5 Hz, 1 H; e-H), 11.89 (d, J = 12.0 Hz, 1 H; f-H).

^{13}C NMR chloroform d$_1$: $\delta = 27.27$, 31.91 (i/k-C), 95.52 (b-C), 114.66, 118.41, 121.05, 125.16, 126.68, 127.40, 129.15, 4/5/6/7/8/9/10-C), 130.59, 131.64 (2/3-C), 137.65 (1-C), 145.92 (c-C), 154.16 (f-C), 190.20 (a-C), 194.80, 201.30 (h/j-C).

Preparation of [3-acetyl-(6,7)-benzo-11-(4′-bromophenyl)-5,8-diazo-2,11-dioxoundeca-2,4,8,10-tetraenato]nickel(II) 4

To the rapidly stirred solution of ligand **3** (2.14 g, 0.005 mole) in methanol (100 cm^3), nickel(II)acetate tetrahydrate (1.24 g, 0.005 mole) was added. The reaction mixture was heated at reflux for 30 min. After cooling a red crystalline product was filtered of, washed with hot water and recrystallized from a mixture chloroform — ethanol (1 : 1). Yield.: 1.62 g (67%).
m.p.: 491 K
elemental analysis: $C_{21}H_{17}BrN_2O_3Ni$
calc.: C 52.12 H 3.54 N 5.79
found.: C 51.95 H 3.46 N 5.82

^{1}H NMR chloroform d$_1$: $\delta = 2.47$ (s, 3 H, g-H), 2.63 (s, 3 H, i-H), 6.18 (d, J = 6.5 Hz, 1 H; b-H), 7.10 (m, 4 H, 6/7/8/9-H), 7.53 (d, J = 8.5 Hz, 2 H; 3-H), 7.66 (d, J = 6.5 Hz, 1 H; c-H), 7.74 (d, J = 8.5 Hz, 2 H; 2-H), 8.34 (s, 1 H; d-H)

The ^{1}H and ^{13}C NMR data gave clear evidence of the non-symmetrical nature of compounds **3** and **4** (confirmed by powder diffraction study). The NMR spectra were recorded on Bruker AMX-500 NMR spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were measured as KBr discs using a Specord M-50 (Carl Zeiss Jena) spectrometer over the range 200–4000 cm^{-1}.

Acknowledgments. The support of Polish Committee of Science Research (KBN, 1115/T09/98/15) and the Foundation of Crystallographic Studies through Carolina H. MacGillary stipend is kindly acknowledged.

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