

CCA-1960

YU ISSN 0011-1643

UDC 546.716

Original Scientific Paper

**Crystal Structure of Polymeric  
Di- $\mu$ (1,3)-Azidodipyridinemanganese(II); [Mn(py)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]**

*Mohamed A. S. Goher*

*Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt*

and

*Franz A. Mautner*

*Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, A-8010  
Graz, Rechbauerstrasse 12, Austria*

Received April 5, 1990

The structure of a 1:2 complex of manganese(II) azide with pyridine has been determined by X-ray crystallography. The crystals are tetragonal and belong to the space group  $I4_1/a$ , with  $a = 1551.7(4)$ ,  $c = 1003.1(1)$  pm and  $Z = 8$ . The structure has been refined to  $R = 0.67$  for 1152 observed  $\text{MoK}\alpha$  diffractometer data. The manganese atom is octahedrally coordinated by six ligand nitrogen atoms at distances of 219.5(5), 221.7(4) and 225.9(3) pm. These octahedra are linked together by the  $\mu(1,3)$ -azido ligands to form a three dimensional network. The azide groups are almost linear and appear to be symmetrical, the N-N distances being 115.1(6) and 117.0(5) pm. The symmetry of the azido ligands is confirmed by disappearance of the  $\nu_3\text{N}_3$  mode from the infrared spectrum.

INTRODUCTION

Since 1964 when the first structural investigation of an azide complex was carried out on the azidopentammincobalt(III) complex  $\text{Co}(\text{NH}_3)_5(\text{N}_3)^{2+1}$ , a lot of structural information on the azido complexes has been accumulated. These structural determinations revealed the variable manner of azide ligand binding giving rise to different modes of bonding, including the end-on bridging<sup>2-8</sup> and end-to-end bridging<sup>9-15</sup> modes.

We recently established, as part of our continuing study of metal pseudohalide complexes of substituted pyridines, that some manganese(II) azide complexes of such ligands possess end-to-end bridging azido groups on the basis of their infrared spectral data.<sup>16</sup> As far as we know, there are only two manganese(II) azide complexes  $[(\text{CO})_3\text{Mn}(\text{N}_3)_3\text{Mn}(\text{CO})_3]^{-17}$  and  $[\text{Mn}(\text{N}_3)]^{4-18}$  that have been studied by means of

X-ray single crystal analysis. In the carbonyl compound the three azide groups operate as  $\mu(1,1)$ -bridging ligands whereas non-bridging azide groups are observed in the second compound.

## EXPERIMENTAL

*Preparation*

An ethanolic solution (10 cm<sup>3</sup>) of pyridine (0.79 g, 10 mmol) was added to MnCl<sub>2</sub>·4H<sub>2</sub>O (0.591 g, 3 mmol) dissolved in 20 cm<sup>3</sup> water and mixed thoroughly. An aqueous solution of NaN<sub>3</sub> (0.357 g, ca 5.5 mmol in 10 cm<sup>3</sup> water) was added in portions with thorough shaking after each addition. The final clear solution was kept in a dark place over several days to produce the complex as colourless crystals, together with some brown powder.<sup>16</sup>

Since the transparent crystals turn opaque in the air, it is convenient to store them in the mother liquor in sealed ampules and filter just before each measurement.

*Anal. Calcd.* for C<sub>10</sub>H<sub>10</sub>N<sub>8</sub>Mn (*M<sub>r</sub>* = 297.18): C 40.42, H 3.40, N 37.70, Mn 18.48%; found: C 40.52, H 3.63, N 37.83, Mn 18.52%. Physical measurements were carried out as described previously.<sup>4</sup>

*X-ray Structure Analysis*

A single crystal of dimensions ca. 0.19×0.20×0.23 mm<sup>3</sup> was centered on a modified STOE four circle diffractometer. After refinement of the cell parameters using diffractometer angles of 98 reflections, the intensity data were collected and processed in the usual way (LP-factor, no absorption correction). Experimental data and parameters are summarized in Table I.

TABLE I

*Experimental parameters and data*

Formula	Mn(py) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> , C <sub>10</sub> H <sub>10</sub> N <sub>8</sub> Mn
Cell constants	<i>a</i> = 1551.7(4) pm, <i>c</i> = 1003.1(1) pm, <i>V</i> = 2415.2×10 <sup>6</sup> pm <sup>3</sup> ,
<i>Z</i>	8
Density (calcd.)	1.634 Mg m <sup>-3</sup>
Space group	<i>I</i> 4 <sub>1</sub> /a (No. 88, second setting)
Radiation	MoK $\alpha$ , $\lambda$ = 71.069 pm
Absorption coefficient	1.02 mm <sup>-1</sup>
F(000)	1208
Scan mode	$\omega$ -scan, $\Delta\omega$ = 1.4°
Collection range	2 $\Theta$ <sub>max</sub> = 65°; <i>h, k, l</i> : 0, 0, 0/23, 23, 15
Temperature	295 K
Unique data measured	2186
Observed data [ <i>F<sub>o</sub></i> ≥ 4 $\sigma$ ( <i>F<sub>o</sub></i> )]	1152
Number of variables	102
<i>R</i> = $\Sigma F_o  -  F_c  / \Sigma F_o $	0.067
<i>R<sub>w</sub></i> = $[\Sigma_w( F_o  -  F_c )^2 / \Sigma_w F_o ^2]^{1/2}$	0.054
Weighting scheme	1.439 $\sigma^2$ ( <i>F<sub>o</sub></i> )

TABLE II

*Atomic coordinates (x 10<sup>4</sup>) and isotropic displacement parameters (pm<sup>2</sup> x 10<sup>-1</sup>).*

Atom	x/a	y/b	z/c	U or U <sub>eq</sub>
Mn	0	0	0	24(1)*
N11	448(3)	836(3)	1624(4)	44(2)*
N12	1041(2)	1109(2)	2169(3)	30(2)*
N13	1621(2)	1388(3)	2776(4)	44(2)*
N1	1727(2)	3286(2)	3971(3)	30(2)*
C1	2088(3)	3773(3)	4904(5)	37(2)*
C2	1621(3)	4233(3)	5822(5)	45(3)*
C3	739(3)	4198(3)	5769(5)	47(3)*
C4	360 (3)	3707(3)	4812(5)	44(3)*
C5	869(3)	3261(3)	3927(5)	35(3)*
H1	2783	3809	4944	72(16)
H2	1942	4616	6572	56(15)
H3	352	4553	6475	74(18)
H4	-334	3667	4746	113(23)
H5	562	2875	3168	88(20)

Asterisks indicate the equivalent isotropic displacement factor U<sub>eq</sub> defined as 1/3 of the trace of the orthogonalized U matrix. The exponent of the isotropic displacement factor takes the form - 8π<sup>2</sup>U sin<sup>2</sup>θ/λ<sup>2</sup>.

Space group and lattice constants gave evidence of isomorphy to the crystal structure of the Cd(py)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> complex.<sup>10</sup> Therefore, the atomic coordinates of the cadmium compound were used as starting values for the structure refinement. Anisotropic displacement parameters were applied to the Mn, C, and N atoms in full-matrix least-squares refinements. The H atoms were geometrically generated and assigned with isotropic displacement parameters in the final refinement cycles.

TABLE III

*Selected bond distances (pm) and bond angles (deg)*

Mn-N11	219.5(5) 2x	N11-Mn-N13	91.4(2) 2x and 88.6(2) 2x
Mn-N13	221.7(4) 2x	N11-Mn-N1	90.0(1) 2x and 89.9(2) 2x
Mn-N1	225.9(3) 2x	N13-Mn-N1	90.7(1) 2x and 89.3(1) 2x
N11-N12	115.1(6)	N11-N12-N13	176.9(4)
N12-N13	117.0(5)	Mn-N11-N12	145.4(4)
N1-C1	132.7(6)	Mn-N13-N12	134.1(3)
N1-C5	133.3(6)	C5- N1-C1	117.5(4)
C1-C2	137.2(7)	N1-C1-C2	123.1(4)
C2-C3	137.1(7)	C1-C2-C3	118.7(4)
C3-C4	135.9(7)	C2-C3-C4	118.8(4)
C4-C5	137.5(7)	C3-C4-C5	119.3(4)
		C4-C5-N1	122.5(4)

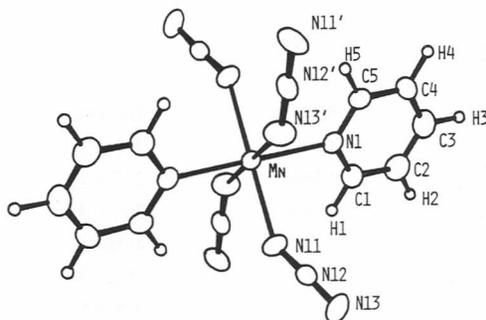


Figure 1. A perspective view of the coordination geometry about the Mn(II) ion in  $[\text{Mn}(\text{py})_2(\text{N}_3)_2]$ . Thermal ellipsoids of the C, N and Mn atoms are drawn at the 50% level. Unlabelled atoms are related by a center of inversion at the metal site.

The SHELX-76<sup>19</sup> and THE XRAY-SYSTEM<sup>20</sup> programs were used for computations, which were carried out on a UNIVAC 1100/81 computer at the Rechenzentrum Graz. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.<sup>21</sup> The final positional parameters are listed in Table II; atom labelling follows that shown in Figure 1. Selected bond distances and bond angles are given in Table III.

Additional material for structure determination is available from the second author on request.

#### DISCUSSION OF THE CRYSTAL STRUCTURE

As illustrated in Figure 1, the manganese atom in the title complex is octahedrally coordinated by six nitrogen atoms; four atoms are end atoms of the azido groups and the other two nitrogen atoms belong to pyridine rings. The  $\text{Mn}(\text{py})_2(\text{N}_3)_2$  complex thus contains both azido groups serving as  $\mu(1,3)$ -bridging ligands as inferred from the infrared spectra.<sup>16</sup> The distances from the manganese atom to nitrogen atoms of the azido groups are Mn-N(11) 219.5(5) pm and Mn-N(13) 221.7(4) pm. These Mn-N distances are longer than the corresponding distances in  $[(\text{CO})_3\text{Mn}(\text{N}_3)_3(\text{CO})_3]^-$  which are variable from 206(2) to 211(2) pm.<sup>17</sup> The three azido groups in the latter complex, however, serve as  $\mu(1,3)$ -bridging ligands.

The present study has shown the title complex to be isomorphous with the corresponding cadmium complex:  $\text{Cd}(\text{py})_2(\text{N}_3)_2$ .<sup>10</sup> However, the Cd-N( $\text{N}_3$ ) distances of 233.6(17) and 235.2(16) pm are slightly longer than those of the Mn-N( $\text{N}_3$ ) bond lengths (Table III). This accounts for the difference in the volume of the cadmium ion as compared to that of the manganese ion. The same is true of the Mn-N(py) bond length [225.9(3) pm] when compared with the corresponding Cd-N(py) distance of 234.9(12) pm. Taking into account the standard deviations, the N-N distances of the azido ligands in the manganese complex [115.1(6) and 117.0(5) pm] are equal to that in the cadmium complex [114.1(21) and 116.7(20) pm].

The Mn-N-N angles of 145.4(4)° and 134.1(3)° are larger than those reported for the isomorphous cadmium complex, that is 139(1)° and 129(1)°. The corresponding values reported are generally around 120°, though they vary over a wide range, and values even larger than those found for the manganese complex have been reported for the [Ca(N<sub>3</sub>)<sub>3</sub>]<sup>-</sup> anion<sup>22</sup> having the same  $\mu(1,3)$ -bridging azido ligands, and  $\alpha$ Pb(N<sub>3</sub>)<sub>2</sub> where the azide group is strongly coordinated to more than one end.<sup>23</sup> In the former, the corresponding values are 180.0(1)° and 170.7(4)°, whereas one value reaches 149.9(3)° in the lead compound.

It is of interest to compare the five M(py)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> complexes (M = Cu<sup>24</sup>, Zn<sup>25</sup>, Cd<sup>10</sup>, Ca<sup>26</sup> and Mn) that have been studied by X-ray crystallography. The zinc complex differs from other four compounds in that it contains a tetrahedral central metal atom and the two azides serve as monodentate ligands. The common feature of the other four complexes is the octahedral geometry around the central atom. However, this octahedral coordination in the copper complex is achieved through two azide groups which are crystallographically distinct with different structural environments. One azide ligand acts as a monodentate whereas the other coordinates asymmetrically to three different metal centers.<sup>24</sup> In this respect, the copper complex differs from both cadmium and manganese complexes having two  $\mu(1,3)$ -bridging azido ligands.

At this point we have to mention the infrared spectrum<sup>16</sup> of the title complex. The manganese(II) complex contains two equivalent azido ligands, and hence we expect a single sharp band associated with the  $\nu_{as}N_3$  mode similar to that reported for the isomorphous cadmium complex.<sup>10</sup> In fact, the spectrum of the manganese(II) complex shows the antisymmetric mode as a broad band centered around 2070 cm<sup>-1</sup>. It seems, therefore, that the  $\nu_{as}$  mode is not a strong diagnosis in case of the symmetrical azides. The symmetry of the azide groups in the manganese complex, as well as other azido complexes, is strongly evidenced by the disappearance of the stretching ( $\nu_s$ ) mode in the region 1380-1280 cm<sup>-1</sup>. In fact, for freshly prepared samples of the manganese complex, we could not detect any absorption due to the  $\nu_s N_3$  mode in the above region. After two days, when the transparent crystals changed to white, this mode appears as a weak band at 1320 cm<sup>-1</sup>. Its intensity increased with time as an indication of increasing decomposition.

*Acknowledgement.* - The authors thank Prof. H. Krischner and Doz. Ch. Kratky for the use of their experimental equipment.

#### REFERENCES

1. G. N. Palenik, *Acta Crystallogr.* **17** (1964) 360.
2. K. D. Karlin, J. C. Hayes, J. P. Hutchinson, and J. Zubieta, *J. Chem. Soc., Chem. Comm.* (1983) 376.
3. J. Pickardt, *Z. Naturforsch.* **B37** (1982) 110.
4. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* **85** (1984) 117.
5. J. Commarmond, P. Plumere', J.-M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, and I. Morgenstern-Badarau, *J. Am. Chem. Soc.* **104** (1982) 6330.
6. M. G. B. Drew, J. Nelson, F. Esho, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.* (1982) 1837.

7. S. Sikorav, I. Bkouche-Waksman, and O. Kahn, *Inorg. Chem.* **23** (1984) 490.
8. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* **89** (1984) 119.
9. V. Mckee, J. V. Dagdigian, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.* **103** (1981) 7000.
10. I. Agrell, *Acta Chem. Scand.* **24** (1970) 3575.
11. R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont and R. Eisenberg, *Inorg. Chem.* **10** (1971) 1289.
12. C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.* **14** (1975) 604.
13. T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.* **17** (1978) 444.
14. Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc.* **101** (1979) 3381.
15. I. Bkouche-Waksman, S. Sikorav and O. Kahn, *J. Crystallogr. Spectrosc. Res.* **13** (1983) 303.
16. M. A. S. Goher and M. A. M. Abu-Youssef, *Acta Chim. Hung.* **124** (1987) 749.
17. R. Mason, A. Rushoime, W. Beck, H. Engelmann, K. Joos, B. Lindenberg and H. S. Smedal, *J. Chem. Soc. Chem. Comm.* (1971) 496.
18. K. Steiner, W. Willing, U. Müller, and K. Dehnicke, *Z. anorg. allg. Chem.* **555** (1987) 7.
19. G. M. Sheldrick, SHELX-76, *A program for crystal structure determination*, University of Cambridge, UK (1976).
20. J. M. Stewart, THE X-RAY SYSTEM, version of 1976, Technical report TR-446, University of Maryland, College Park, USA (1976).
21. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1973 p. 99, 149.
22. F. A. Mautner, H. Krischner and Ch. Kratky, *Z. Kristallogr.* **175** (1986) 105.
23. C. S. Choi and H. P. Boutin, *Acta Crystallogr.* **B25** (1969) 982.
24. I. Agrell, *Acta Chem. Scand.* **23** (1969) 1667.
25. I. Agrell, *Acta Chem. Scand.* **24** (1970) 1247.
26. F. A. Mautner, H. Krischner, and Ch. Kratky, *Monatsh. Chem.* **118** (1987) 567.

### SAŽETAK

Kristalna struktura polimernog di- $\mu(1,3)$ -azidodipiridinmangan(II);  
 $[\text{Mn}(\text{py})_2(\text{N}_3)_2]$

Mohamed. A. S. Goher i Franz A. Mautner

Kristali (1:2) kompleksa mangan(II)-azida s piridinom spadaju u tetragonsku prostornu grupu  $I4_1/a$ ;  $a = 1551,7(4)$ ,  $c = 1003,1(1)$  pm;  $Z=8$ . Struktura je određena metodom rendgenske difrakcije ( $\text{MoK}\alpha$ ); uočnjavano je 1152 opaženih refleksa do  $R=0,067$ . Atom mangana koordiniran je oktaedarski sa šest dušikovih atoma; udaljenosti Mn-N iznose 219,5(5), 221,7(4) i 225,9(3) pm. Oktaedri su međusobno povezani  $\mu(1,3)$ -azido ligandima u trodimenzijnsku mrežu. Udaljenosti među atomima dušika u azido-grupama iznose 115,1(6) i 117,0(5) pm.