Inorganica Chimica Acta, 46 (1980) L47–L50
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Adenine N(1)-Oxide Complexes with Cobalt(II), Nickel(II) and Copper(II) Perchlorates*

CHESTER M. MIKULSKI

Department of Chemistry and Physics, Beaver College, Glenside, Pa. 19038, U.S.A.

FRANK J. IACONIANNI, LOUIS L. PYTLEWSKI

Department of Chemistry, Drexel University, Philadelphia, Pa. 19104, U.S.A.

ANTHONY N. SPECA

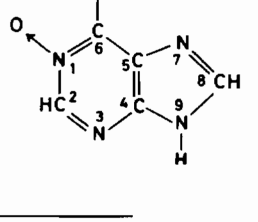
USI Chemicals Co., Research Division, Cincinnati, Ohio 45237, U.S.A.

and NICHOLAS M. KARAYANNIS

Amoco Chemicals Corporation, Naperville, Ill. 60540, U.S.A.

Received January 16, 1980

Following our recent synthetic and characterization studies of adenine (adH) complexes with 3d metal perchlorates [2], we extend our work to the study of the corresponding complexes of adenine N(1)-oxide(adH-NO; I). Thus far, Co^{2+}, Ni^{2+} and Cu^{2+} perchlorate complexes with the N-oxide ligand have been isolated by the following synthetic procedure and characterized: 1.4 mmol metal(II) perchlorate is dissolved in a mixture of 15 ml triethyl orthoformate (teof) and 35 ml ethanol. Then, 2.5 mmol adH-NO are added, and the mixture is refluxed for 48 hr. Under these conditions, $Co(ClO_4)_2$ forms a brick red solid complex, which starts precipitating after *ca.* 2 hr of refluxing and its amount gradually increases as refluxing continues. After 48 hr of refluxing, the volume of the reaction mixture is reduced to about one-half the original volume, and the new complex is separated by filtration, washed with anhydrous diethyl ether and stored in an evacuated desiccator over anhydrous $CaCl_2$. Analytical data indicate that this complex is of the $Co(adH\text{-}NO)_2(ClO_4)_2 \cdot 2C_2H_5OH$ type [found(calc.)%: C, 25.42(25.78); H, 3.65(3.40); N, 21.55(21.47); Co, 8.87(9.04); Cl, 11.17(10.87); yield 72% of the theoretical].



(I)

With Ni^{2+} and Cu^{2+} perchlorates, small amounts of precipitate (golden-orange for M = Ni and maroon for M = Cu) started depositing after 1–2 hr of refluxing. However, upon continuation of refluxing these precipitates were gradually dissolved in the mother liquor and replaced by small amounts of green-colored precipitates (light green for M = Ni and olive-green for M = Cu) at the end of the 48 hr. The amounts of these green precipitates were increased by reducing the volume of the supernatant to about one-half its original volume, and the new complexes were separated by filtration, washed and dried in the manner described above. Analytical data indicate that these complexes involve both neutral (adH-NO) and monodeprotonated (ad-NO) adenine N(1)-oxide ligands, being of the following types: $Ni(ad\text{-}NO)(adH\text{-}NO)(ClO_4) \cdot 2C_2H_5OH$: Found (Calc.) %: C, 30.12(30.47); H, 3.71(3.84): N, 25.80(25.38); Ni, 10.70(10.64); Cl, 6.79(6.42); and $Cu_2(ad\text{-}NO)_2(adH\text{-}NO)(ClO_4)_2$: Found (calc.)%: C, 22.86(23.18); H, 1.93(1.69; N, 26.75(27.03); Cu, 16.40(16.34); Cl, 9.57(9.12). Both of the preceding complexes were obtained in yields of *ca.* 55% of the theoretical. It should be pointed out here that the golden-orange and maroon solids precipitated at the early stages of refluxing of the mixture of Ni^{2+} of Cu^{2+} (respectively) perchlorate with adH-NO in teof-ethanol, are assumed to be the analogs of the Co^{2+} complex herein reported, *i.e.*, of the $M(adH\text{-}NO)_2(ClO_4)_2 \cdot xC_2H_5OH$ (M = Ni, Cu) type. We are currently involved in attempts at the preparation of quantities of these compounds, sufficient for characterization.

The three new complexes reported are insoluble in organic media and were characterized by means of solid-state spectral and magnetic studies; pertinent data are shown in Table I, whilst some additional spectral features are discussed below. The ir spectrum of the Co^{2+} complex (Nujol mull) is characterized by triply split ν_3 (1137vs, 1095vvs, 1052vs,b) and ν_4 (641w, 628m, 621m,sh) ClO_4 bands (in cm^{-1}), thus indicating the simultaneous presence of ionic (T_d symmetry) ClO_4^- and unidentate coordinated $-OClO_3$ (C_{3v} symmetry) ligands [3, 4]. In contrast, the Ni^{2+} and Cu^{2+} complexes exhibit doubly split ν_3 (1100vs,b, 1045vs,sh for M = Ni; 1092vvs, 1056vs for M = Cu) and ν_4 (619m, 611m for M = Ni; 632m, 614m,sh for M = Cu) perchlorate bands; these can be interpreted in terms of the exclusive presence of unidentate coordinated perchlorato ligands [3, 4]. Ligand absorption in the ν_1 and ν_2 (ClO_4) regions prevents the detection of ir-active bands due to the coordinated $-OClO_3$ ligands.

Previous studies of adenine N(1)-oxide complexes with CuX_2 (X = Cl, ClO_4, ½SO_4) and of

---

*See ref. 1.

TABLE 1. Spectral and Magnetic Data for Adenine N(1)-oxide Complexes with M^{2+} Perchlorates.[a]

Pertinent ir data, cm^{-1}	adH-NO	M = Co	M = Ni	M = Cu
NH_2 sym in-plane deformation	1663ms	1670s	1660ms	1656s
ν_{N-O} + NH_2 asym out-of-plane deformation	1272m	1273ms	1270w	
	1240m	1238ms	1236m	1248m
		1195ms,b	1198s	1199s
$\nu_{M-O}(N-O)$		361w	377m	461s, 421m,sh
$\nu_{M-O}(C_2H_5OH)$		347w,b	355mw	
$\nu_{M-O}(OClO_3)$		312w,b	307mw	372ms
ν_{M-N}		255w, 232w	258w, 234w	319m, 302m, 271m
Solid-state electronic spectra, nm				
d–d transition bands		468m, 512m, 990w,sh, 1300w,b	395s, 625m, 747m, 1025w,b, 1265w,b	617sh, 660s,b
Magnetic data (298 °K)				
$10^6\chi_M^{cor}$, cgsu		10,930	4600	1174
μ_{eff}, μB		5.13	3.33	1.68

[a] Ir and electronic spectra were obtaine on Nujol mulls on the complexes.

Cu(ad-NO)$_2$ [5], as well as stability constant studies of the complexes of this ligand with 3d M^{2+} ions (M = Mn through Zn) [6], led to the conclusion that adH-NO or ad-NO function as bidentate ligands, coordinating through the NH_2 (or =NH in the monodeprotonated ligand) and N(7) nitrogen atoms without any involvement of the N(1)–O oxygen in coordination [5, 6]. On the other hand, adenosine N(1)-oxide has been considered as having the tendency to chelate through the N(1)–O oxygen and the NH_2 nitrogen [6–8], although it has been also concluded that the N(7) nitrogen site is the most favored site for bonding in this ligand [9, 10]. Examination of the NH_2 symmetric in-plane and asymmetric out-of-plane deformation modes in the ir spectra of free adH-NO and of the complexes herein reported (Table I), indicates that almost negligible shifts of these bands occur upon metal complex formation. These features tend to rule out the participation of the NH_2 nitrogen in coordination [9, 11–13]. On the other hand, all the new complexes show a medium-to-strong or strong band at 1199–1195 cm^{-1}, while adH-NO shows only a weak absorption at 1210 cm^{-1} ($A'\delta_{CH}$ [14]). The new band at 1199–1195 cm^{-1} in the spectra of the complexes cannot be attributed to either the above $A'\delta_{CH}$ band of the ligand, which tends to undergo positive frequency shifts upon metal complex formation [14, 15], or to a substantial shift of the NH_2 asym out-of-plane deformation mode, since the NH_2 sym in-plane deformation band does not undergo such a shift. Hence, it is most likely that this new absorption is due to a substantial shift of the ν_{N-O} mode (which is probably associated with the band at 1272 cm^{-1} in the spectrum of the free ligand [16], partially overlapping with the NH_2 asym out-of-plane deformation absorption at 1240 cm^{-1}) to lower wavenumbers. This is indicative of coordination of at least part of the ligands through the N(1)–O oxygen [17, 18]. The complete disappearance of the band at 1272 cm^{-1} in the spectrum of the Cu^{2+} complex suggests that all the adenine N(1)-oxide ligands in this complex are coordinated through the N(1)-O oxygen; whereas the spectra of the Co^{2+} and Ni^{2+} new complexes are characterized by bands attributable to both uncoordinated (1273–1270 cm^{-1}) [16] and coordinated (1198–1195 cm^{-1}) [17, 18] N(1)-O oxygen sites. Coordination through oxygen is also supported by the tentative identification of low-frequency ir bands attributable to ν_{M-O} (N-oxide) vibrational modes [17, 19–21]. Bands attributable to ν_{M-N} (N-bonded ligands) [2, 22, 23], as well as ν_{M-O} ($-OClO_3$) [2, 24] and ν_{Co-O} or ν_{Ni-O} (ethanol) [2, 25], modes, were also identified in the ir spectra of the new complexes (Table I). The location of the various metal–ligand bands favors coordination number six for M = Co, Ni, and coordination number four for M = Cu [19–25]. The Co^{2+} and Ni^{2+} complexes show the ν_{OH} mode of coordinated ethanol at 3360–3330 cm^{-1} [26].

The d–d transition spectra of the Co^{2+} and Ni^{2+} complexes (Table I) are consistent with low-symmetry hexacoordinated configurations. An approximate Dq value of 873 cm^{-1}, calculated from the spectrum of the Ni^{2+} complex, is not incompatible with a NiN_2O_4 absorbing species (the four oxygens corresponding to one $-OClO_3$, one N-oxide and two ethanol ligands; *vide infra*) [17, 22]. The occurrence of the split d–d band maxima at 617 and 660 nm in the spectrum of the Cu^{2+} complex can be attributed to a square-planar configuration with adenine N(1)-oxide functioning as a bidentate O,N-ligand [17, 22].

The ambient temperature magnetic moment of the Cu^{2+} complex (1.68 μB) is somewhat low for magnetically normal Cu^{2+} compounds, and reminiscent of the magnetic behavior of several compounds involving the quadruple-bridged $[Cu(adH)_4Cu]^{4+}$ cationic species, in which adenine functions as a bidentate bridging ligand, coordinating through the N(3) and N(9) nitrogen atoms [27]; such an arrangement of the four bridging adenine ligands between two Cu^{2+} ions leads to antiferromagnetic exchange even at room temperature, at which moments of 1.5–1.7 μB are observed [2, 22, 28–30]. The new Co^{2+} and Ni^{2+} complexes exhibit normal ambient temperature magnetic moments. The moment of the Co^{2+} complex (5.13 μB) is within the limits of the "octahedral" region for cobaltous compounds, while that of the Ni^{2+} compound (3.33 μB) is slightly higher than the upper limit (3.30 μB) of the corresponding region for Ni^{2+}; this is not unusual for hexacoordinated complexes of this metal ion with aromatic amine N-oxides [31].

The insolubility of the new complexes in organic media may be taken as suggestive of bi- or polynuclear structures, with part or all of the adenine N(1)–oxide ligands present acting as bidentate, bridging, O,N-bonded, coordinating through the N(1)-O oxygen and one of the imidazole nitrogens (N(7) or N(9)). As regards the actual nitrogen binding site of the ligand, it should be noted that the parent base (adenine) shows a pronounced tendency to use the N(9) site in its coordination [27, 32–34]; in fact, coordination through the N(7) nitrogen has been established only for $Zn(adH_2)Cl_3$, which contains the monoprotonated adeninium cation [35]. Among other biologically important purines, guanine and xanthine also show the tendency to coordinate through the N(9) nitrogen [36, 37], while theophylline prefers coordination through the N(7) site [38, 39]. As far as established structures of metal complexes with bidentate bridging purines are concerned, most common appears to be coordination of the ligands either through the N(3), N(9) [27, 32–34] or the N(1), N(7) [40, 41] sites, although quite recently a Hg^{2+} complex with bidentate, bridging, N(7), N(9)-bonded adenine was also reported [42]. Bridging of adenine N(1)-oxide through the N(1)-O oxygen and the N(9) nitrogen sites would not be inconceivable; nevertheless, the fact that no metal complexes with N(1), N(9)-bonded bridging purine ligands have been established, combined with the previously ascertained tendency of adenine N(1)-oxide to use the N(7) nitrogen as ligand site [5, 6, 9, 10], can be considered as favoring the coordination of the bridging ligands in the complexes herein reported through the N(1)-O oxygen and the N(7) nitrogen. It is worth noting, in this connection, that the substitution of the aza group in the 1 ring position with an N–O group would significantly alter the electron density distribution around the rest of the ring nitrogen atoms (N(3), N(7) and N(9)), relative to that in unsubstituted adenine [17, 43].

On the basis of the overall evidence presented, a triple-bridged, binuclear structure of the $[(O_3ClO)Cu(ad\text{-}NO)_2(adH\text{-}NO)Cu(OClO_3)]$ type, with exclusively bidentate, bridging, O,N-bonded adenine N(1)-oxide ligands, would account for the subnormal room temperature paramagnetism of the new Cu^{2+} complex. The Co^{2+} and Ni^{2+} complexes appear magnetically normal at room temperature; this does not preclude bridged structures for these compounds, since several magnetically normal (at room temperature) bi- or poly-nuclear complexes of these metal ions, with such bridging ligands as diazines [44] and aromatic amine N-oxides [17], are known. Thus, binuclear structures of the types $[(C_2H_5OH)_2(O_3ClO)(adH\text{-}NO)Co(adH\text{-}NO)_2Co(adH\text{-}NO)(OClO_3)(C_2H_5OH)_2](ClO_4)_2$ and $[C_2H_5OH)_2(O_3ClO)(ad\text{-}NO)Ni(adH\text{-}NO)_2Ni(ad\text{-}NO)(OClO_3)(C_2H_5OH)_2]$, with both terminal unidentate and bridging bidentate adenine N(1)–oxide ligands, may be considered as likely for these complexes. Regarding the probable bonding site of the terminal adenine N(1)-oxide ligands in the preceding complexes, nitrogen is favored over oxygen, since the ir spectra of the Co^{2+} and Ni^{2+} complexes show ν_{N-O} bands attributable to both uncoordinated and coordinated N(1)-O oxygen sites (*vide supra*).

References

1 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Abstracts, Joint Am. Chem. Soc./Chem. Soc. Japan Chem. Congress*, Honolulu, Hawaii, April 1–6, 1979; No. INOR 33.

2 *Idem, Inorg. Chim. Acta, 37,* L551 (1979).

3 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc., 3091* (1961); B. J. Hathaway, D. G. Holah and M. Hudson, *ibid.*, 4586 (1963).

4 A. E. Wickenden and R. A. Krause, *Inorg. Chem., 4,* 404 (1965); S. F. Pavkovic and D. W. Meek, *ibid., 4,* 1091 (1965); M. E. Farago, J. M. James and V. C. G. Trew, *J. Chem. Soc., A,* 820 (1967).

5 R. Weiss and H. Venner, *Hoppe Seyler's Z. physiol. Chem., 350,* 230 (1969).

6 D. D. Perrin, *J. Am. Chem. Soc., 82,* 5642 (1960).

7 H. Sigel and H. Brintzinger, *Helv. Chim. Acta, 47,* 1701 (1964); H. Sigel and B. Prijs, *ibid., 50,* 2357 (1967).
8 H. Sigel, *Helv. Chim. Acta, 48,* 1519 (1965).
9 N. Hadjiliadis and T. Theophanides, *Inorg. Chim. Acta, 16,* 67 (1976).
10 P. C. Kong and T. Theophanides, *Inorg. Chem., 13,* 1984 (1974).
11 J. Brigando and D. Colaitis, *Bull. Soc. Chim. France,* 3445, 3449 (1969).
12 T. Fujita and M. Ishino, *Nippon Kagaku Kaishi,* 1480 (1974); T. Fujita and T. Sakaguchi, *Chem. Pharm. Bull., 25,* 1055, 2419 (1977).
13 R. B. Simpson, *J. Am. Chem. Soc., 86,* 2059 (1964); M. J. Clarke, *ibid., 100,* 5068 (1978); S. Mansy, J. P. Frick and R. S.Tobias, *Biochim. Biophys. Açta, 378,* 319 (1975).
14 A. Lautié and A. Novak, *J. Chim. Phys. Physicochim. Biol., 65,* 1359 (1968); *68,* 1492 (1971).
15 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, to be published.
16 R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc., 79,* 2233 (1957).
17 N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973); N. M. Karayannis, A. N. Speca, D. E. Chasan and L. L. Pytlewski, *ibid., 20,* 37 (1976).
18 Y. Kakiuti, S. Kida and J. V. Quagliano, *Spectrochim. Acta, 19,* 201 (1963); L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta, 10,* 177 (1974).
19 A. D. van Ingen Schenau, W. L. Groeneveld and J. Reedijk, *Spectrochim. Acta, 30A,* 213 (1974); A. D. van Ingen Schenau, C. Romers, D. Knetsch and W. L. Groeneveld, *ibid., 33A,* 859 (1977).
20 A. T. Hutton and D. A. Thornton, *J. Mol. Struct., 39,* 33 (1977).
21 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 33,* 3185 (1971).
22 M. A. Guichelaar and J. Reedijk, *Recl. Trav. Chim., 97,* 295 (1978).
23 N. B. Behrens, D. M. L. Goodgame and Z. Warnke, *Inorg. Chim. Acta, 31,* 257 (1978).
24 J. R. Ferraro and A. Walker, *J. Chem. Phys., 42,* 1273, 1278 (1965).
25 C. M. Mikulski, L. S. Gelfand, L. L. Pytlewski, J. S. Skryantz and N. M. Karayannis, *Inorg. Chim. Acta, 21,* 9 (1977).
26 V. Imhof and R. S. Drago, *Inorg. Chem., 4,* 427 (1965); P. W. N. M van Leeuwen, *Recl. Trav. Chim., 86,* 247 (1968).
27 A. Terzis, A. L.Beauchamp and R. Rivest, *Inorg. Chem., 12,* 1166 (1973).
28 R. W. Duerst, S. J. Baum and G. F. Kokoszka, *Nature, 222,* 665 (1969); B. Jeżowska-Trzebiatowska, H. Kozłowski and A. Antonóv, *Bull. Acad. Polon. Sci., Ser. Sci. Chim., 22,* 31 (1974).
29 D. B. Brown, J. R. Wasson, J. W. Hall and W. E. Hatfield, *Inorg. Chem., 16,* 2526 (1977); D. B. Brown, J. W. Hall, H. M. Helis, E. G. Walton, D. J. Hodgson and W. E. Hatfield, *ibid., 16,* 2675 (1977).
30 K. A. Price and D. M. L. Goodgame, *Nature, 220,* 783 (1968); M. V. Hanson, C. B. Smith, G. D. Simpson and G. O. Carlisle, *Inorg. Nucl. Chem. Lett., 11,* 225 (1975); T. Asakawa, M. Inoue, K. Hara and M. Kubo, *Bull. Chem. Soc. Japan, 45,* 1054 (1971).
34 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7,* 1835 (1968).
32 D. J. Hodgson, *Prog. Inorg. Chem., 23,* 211 (1977).
33 E. Sletten, *Acta Crystallogr., B25,* 1480 (1969).
34 P. de Meester and A. C. Skapski, *J. Chem. Soc., Dalton Trans.,* 2400 (1972); *424,* 1596 (1973).
35 L. Srinivasan and M. R. Taylor, *Chem. Commun.,* 1668 (1970); M. R. Taylor, *Acta Crystallogr., B29,* 884 (1973).
36 J. A. Carrabine and M. Sundaralingam, *J. Am. Chem. Soc., 92,* 369 (1970); *idem. Biochemistry, 10,* 292 (1971); M. Sundaralingam and J. A. Carrabine, *J. Mol. Biol., 61,* 287 (1971).
37 L. G. Marzilli, L. A. Epps, T. Sorrell and T. J. Kistenmacher, *J. Am. Chem. Soc., 97,* 3351 (1975).
38 T. J. Kistenmacher, D. J. Szalda, C. C. Chiang, M. Rossi and L. G. Marzilli, *Inorg. Chem., 17,* 2582 (1978), and refs. therein.
39 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio and M. Tiripicchio Camellini, *Transition Met. Chem., 4,* 221 (1979).
40 C. J. L. Lock, R. A. Speranzini, G. Turner and J. Powell, *J. Am. Chem. Soc., 98,* 7865 (1976).
41 P. de Meester, D. M. L. Goodgame, A. C. Skapski and Z. Warnke, *Biochim. Biophys. Acta, 324,* 301 (1973).
42 L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, *J. Am. Chem. Soc., 101,* 2765 (1979).
43 A. R. Katritzky and F. J. Swinbourne, *J. Chem. Soc.,* 6707 (1965).
44 J. R. Ferraro, J. Zipper and W. Wozniak, *Appl. Spectroscopy, 23,* 160 (1969).