Polish J. Chem., **77**, 1049–1052 (2003) **COMMUNICATION**

Synthesis and Properties of the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I) Complexes with Indazole and 5-Aminoindazole

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(Received February 7th, 2003; revised manuscript April 7th, 2003)

The coordination chemistry of pyrazole and its derivatives has been the subject of many investigations. The complexes have been studied both in the aqueous solutions [1–9] and in the solid state [10–14]. It has been proved that the relatively high stability of the complexes in solutions has been caused by the considerable π-acceptor properties of the ligands. Conjugation of the pyrazole and benzene rings increases delocalization of π-electrons. This fact influences donor-acceptor properties of the heterocyclic ring.

For this reason, the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I) complexes of indazole and 5-aminoindazole were prepared in the solid state and investigated by elemental analysis, IR and *far*-IR spectroscopy, ligand field spectra and magnetic susceptibility data. Unfortunately, it was impossible to study the stability of complexes in a water solution because of too low solubility of the ligands shown in Fig. 1.

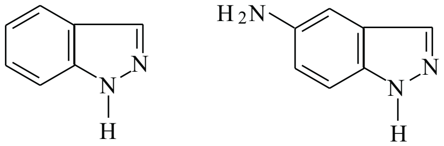

Figure 1. Indazole and 5-aminoindazole.

Ruthenium(III) indazole complexes have been intensively studied, because they show antitumor activities [15–17], as non-platinum antitumor agents.

In the experimental studies the following high purity reagents were used without further purification: indazole (Aldrich), m.p. 147–149°C , and 5-aminoindazole (Aldrich), m.p. 175–178°C. Other chemicals were from POCh-Gliwice. The complexes were prepared as described below: 2 mmole of metal nitrate was dissolved in 20 cm^3 of hot mixtures of methanol-water (1:1). This solution was added under stirring to a solution of 10 mmoles of ligand in hot methanol. The complexes precipitated immediately. They were washed with methanol and dried in a vacuum desiccator.

Elemental analyses of the complexes were performed on a Model 240 Perkin Elmer Analyzer. The IR spectra in the range 4000–400 cm^{-1} were made using KBr pellets of samples, while those in the *far*-IR range 400–100 cm^{-1} were made in nujol. The IR spectra were performed on a Specord M80, and those of *far*-IR on a Digital FTS-60 spectrophotometer. The reflectance spectra were made using $LiCO_3$ pellets on Carry 500 UV-VIS-NIR spectrophotometer.

The resolution processing of the weakly resolved bands in the diffuse reflectance spectra of Cu(II) complexes has been performed by applying the variable digital filter method described by Bierman and Ziegler [18] and used successfully by others [19–21] and us [22–23]. The computer program by J. Myrczek [19] was used to this purpose.

Magnetic susceptibility measurements at room temperature were made on Magnetic Susceptibility Balance from Sherwood Scientific. The effective magnetic moments were calculated as $\mu = 2.828\sqrt{\chi T}$ (B.M.), where χ is the molar susceptibility of sample.

The elemental analyses results of all the studied complexes are in agreement with suggested stoichiometries within 1%. The complexes were characterized by IR and *far*-IR spectroscopy. Table 1 summarizes the most important spectral bands and proposed assignments of the free ligands and their complexes.

Strong absorption bands occur in the range 1620–1500 cm^{-1}. These absorptions involve stretching ν(C=N) and ν(C=C) vibrations [24]. The bands in the spectra of the complexes are shifted to lower frequencies, presumably due to the formation of a bond between the ring nitrogen atom and the metal ion.

Table 1. Infrared absorption bands of indazole (in), 5-aminoindazole (ain) and their complexes in the range 4000–100 cm^{-1}.

Compound	ν(OH)	$\nu(NH_2)$	ν(NH)	ν(CH)	$\delta(NH_2)$	ν(C=N, C=C)	$\nu(NO_3)$	Other bands
Indazole			3175s	2950s		1621s, 1503m		
$[Co(in)_4(NO_3)_2]$			strong broad band at *ca.* 3310			1510s, 1482m	1380s 1352a	216s
$[Ni(in)_4(NO_3)_2]$			strong broad band at *ca.* 3240			1511m, 1484m	1380s 1343s	217s
$[Cu(in)_4(NO_3)_2]$			3128s	2880s		1511m, 1482s	1376s 1354s	238s
$[Zn(in)_3(H_2O)_3](NO_3)_2$	3540m, br		strong broad band at *ca.* 3300			1513m, 1480m	1384s	213s
$[Cd(in)_3(H_2O)_3](NO_3)_2$	3540m, br		3198s	3022s		1508m, 1475m	1384s	219s
$[Ag(in)_2]NO_3$			3180s	2970s		1508m, 1447m	1384s	230s
5-Aminoindazole		3352s	3210s	2930s	1640s	1576s, 1512s		
$[Co(ain)_3(H_2O)_3](NO_3)_2$	3550m, sh	strong broad band at *ca*. 3350			1640s	1552s, 1496s	1384s	222s 267s
$[Ni(ain)_2(NO_3)_2]$		3310s	3215s	2935s	1625m	1548s, 1504s	1375s 1342s	214s 276s

Table 1 (continuation)

$[Cu(ain)_2(NO_3)_2]$		strong broad band at *ca.* 3250			1630m	1552s, 1460s	1380s 1350s	256s
$[Zn(ain)_3(H_2O)_3](NO_3)_2$	3550br	3350s	3210s	2930s	1640s	1552s, 1476s	1384s	275s
$[Cd(ain)_2(NO_3)_2]$		3340s	3220s	2930s	1610s	1548s, 1500s	1380s 1360s	288s
$[Ag(ain)]NO_3$		3345s	3234s	2922s	1635m	1515s, 1486s	1384s	281s

s – strong, m – medium, w – weak, br – broad, sh – shoulder.

In the 5-aminoindazole complexes of Ni(II), Cu(II), Cd(II) and Ag(I), a distinct displacement toward lower frequencies of strong bands at 1640 cm^{-1} and 3352 cm^{-1} [24] is observed. It may be due to the formation of a bond between a nitrogen atom and the metal cation. The observed shift may also be a result of hydrogen bonds formation. After planned X-ray studies, this problem should be solved.

Strong $\nu(NO_3)$ absorption bands occur in the spectra of all the complexes. In some cases these bands are split, thus, suggesting that nitrate anion is coordinated to metal ion in these complexes [25].

A comparison of the *far*-IR spectra of the ligands and their complexes reveals that the new strong bands, that are not present in the ligands, appear in the spectra of the complexes. These bands can be attributed to the M–N stretching vibrations [26].

The electronic absorption bands and their assignments for Co(II), Ni(II) and Cu(II) complexes of indazole are shown in Table 2. The spectra of the 5-aminoindazole complexes were impossible to study because ligand shows strong absorption in the visible range. The bands of electronic spectra of Co(II) and Ni(II) complexes correspond to the d-d electron transitions in the ligand field with octahedral symmetry [27].

Table 2. Electronic bands (cm^{-1}) and magnetic moments (B.M.) of indazole (in) and 5-aminoindazole (ain) complexes.

Complex	Electronic bands and their assignments		$\mu_{eff.}$
$[Co(in)_4(NO_3)_2]$	9480	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$	4.77
	20660	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$[Ni(in)_4(NO_3)_2]$	10820	$^3A_{2g} \rightarrow {}^3T_{2g}$	3.17
	17430	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
	27720	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
$[Cu(in)_4(NO_3)_2]$	11540	$^2B_{1g} \rightarrow {}^2A_{1g}$	2.07
	13640	$^2B_{1g} \rightarrow {}^2B_{2g}$	
	18060	$^2B_{1g} \rightarrow {}^2E_g$	
$[Co(ain)_3(H_2O)_3](NO_3)_2$	Strong absorption of the ligand		4.84
$[Ni(ain)_2(NO_3)_2]$			3.08
$[Cu(ain)_2(NO_3)_2]$			2.18

In the case of the Cu(II) complexes, the single asymmetric band was resolved with the digital filter method. The band under digital filtration process resulted in three component peaks. The positions of the bands indicate a pseudo-octahedral configuration with a tetragonal distortion with the following one electron orbital sequence: $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}\, d_{yz}$. It is in agreement with the general observations that Cu(II) d-d transitions are close in energy [28,29].

The values of the room temperature effective magnetic moments of Co(II), Ni(II) and Cu(II) complexes (Table 2) are in the acceptable ranges for the presence of three unpaired electrons of Co(II) d^7, two unpaired electrons of Ni(II) d^8 and single unpaired electron of Cu(II) d^9, in the complexes with coordination number six [27,28]. Thus, it can be concluded that all the complexes of the divalent metal ions have coordination number six with pseudo-octahedral environment of central ion.

REFERENCES

1. Crow D.R. and Westwood J.V., *J. Inorg. Nucl. Chem.,* **30**, 179 (1968).
2. Musgrave T.R. and Humburg E.R., *J. Inorg. Nucl. Chem.,* **30**, 2229 (1968).
3. Lenarcik B. and Wiśniewski M., *Roczn. Chem.,* **49**, 497 (1975).
4. Lenarcik B. and Nabiałek K., *Roczn. Chem.,* **51**, 417 (1977).
5. Lenarcik B. and Gabryszewski M., *Roczn. Chem.,* **51**, 2001 (1977).
6. Poddar S.N., Ghosh S., Bhattacharya S.M. and Roy-Chaudhuri S., *J. Inorg. Nucl. Chem.,* **39**, 739 (1977).
7. Lenarcik B., Nabiałek K. and Gabryszewski M., *Polish J. Chem.,* **52**, 401 (1978).
8. Lenarcik B. and Kulig., *Polish J. Chem.,* **52**, 2089 (1978).
9. Barszcz B. and Kulig J., *Rev. Roum. Chim.,* **44**, 131 (1999).
10. Reedijk J., *Rec. Trav. Chim*., **88**, 1451 (1969).
11. Reedijk J., *Rec. Trav. Chim.,* **89**, 605 (1970).
12. Nicholls D. and Warburton B.A., *J. Inorg. Nucl. Chem.,* **32**, 3871 (1970).
13. Nicholls D. and Warburton B.A., *J. Inorg. Nucl. Chem.,* **33**, 1041 (1971).
14. Trofimenko S., *Chem. Rev.,* **72**, 497 (1972).
15. Peti W., Pieper T. and Sommer M., *Eur. J. Inorg. Chem.,* **9**, 1551 (1999).
16. Clarke J.M., Zhu F. and Frasca D.R., *Chem. Rev.,* **99**, 2511 (1999).
17. Vashist Gopel Y.N. and Kondapi A.K., *J. Biosci.,* **26**, 271 (2001).
18. Bierman G. and Ziegler H., *Anal. Chem.,* **58**, 536 (1986).
19. Myrczek J., *Spectr. Letters,* **23**, 1027 (1990).
20. Staszak Z., Golonka-Cieslak M. and Raczko M., *Spectr. Letters*, **25**, 349 (1992).
21. Adach A., Janyst J. and Golonka-Cieslak M., *Spectr. Letters*, **28**, 1259 (1995).
22. Gabryszewski M., *Polish J. Chem*., **72**, 2519 (1998).
23. Gabryszewski M. and Wieczorek B., *Spectr. Letters*, **33**, 23 (2000).
24. Silverstein R.M., Bassler G.C. and Morill T.C., *Spectrometric Identification of Organic Compounds,* John Wiley, NY (1991).
25. Haasnoot J.G., Vos G. and Groeneweld W.L., *Z. Naturforsch*., **32b**, 1421 (1977).
26. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Chemistry*, John Wiley, NY (1978).
27. Cotton F.A. and Wilkinson G., *Advanced Inorganic Chemistry, John Wiley, NY (1970).*
28. Hathaway B.J., *Comprehensive Coordination Chemistry, Pergamon Press, Oxford (1987).*
29. Lever A.B.P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1984).