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Studies of Chelates with Heterocyclic Ligands

III. Coordination Compounds of Transition Metals with 5-Aminoquinoxaline

OTTO DAHL and PER HALFDAN NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

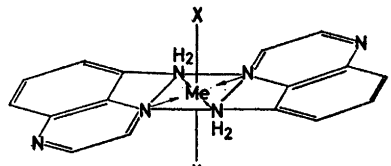
Synthesis and properties of transition metal complexes with the new ligand 5-aminoquinoxaline are reported. Metal(II) chlorides form coordination compounds of the general formulas Me(5-aminoquinoxaline)$_2$Cl$_2$ (Me = Fe(II), Co(II), and Ni(II)) and Me(5-aminoquinoxaline)Cl$_2$ (Me = Cu(II), Cd(II), and Pd(II)). They possess only little stability and are decomposed when dissolved in water. The magnetic properties and reflectance spectra are consistent with the presence of a distorted octahedral configuration in the cobalt(II) and nickel(II) complexes. The infrared spectra of the complexes are discussed with special emphasis on the NH_2 and C—N vibrations. Compounds of cobalt(II), nickel(II), and copper(II) perchlorates with 5-aminoquinoxaline have also been prepared. The infrared spectra suggest that the perchlorate ions are not coordinated to the central metal ion.

Increasing attention has recently been given to the formation of coordination compounds of various metal salts with 8-aminoquinoline (8-AQ),[1–6] however, the corresponding coordination compounds with 5-aminoquinoxaline (5-AQx) have not yet been studied. The present work was initiated with a view to find out whether the behaviour of 8-AQ could be generalised to 5-AQx as well.

5-AQx in absolute ethanol forms complexes with the general formula Me(5-AQx)$_2$Cl$_2$ (type I) where Me = Fe(II), Co(II), and Ni(II). The preparation of the Fe(II) and Co(II) complexes was carried out in a nitrogen atmosphere in order to prevent oxidation. The Co(II) and Ni(II) complexes had pale colours at that of the corresponding complexes of 8-AQ,[1–6] whereas the Fe(II) complex was intense lilac. No complexes could be isolated with $CrCl_3$ or $MnCl_2$ as observed by Fanning and Taylor [4] for 8-AQ.

From ethanol-water mixtures, complexes with the general formula Me(5-AQx)Cl$_2$ (type II), where Me = Cu(II), Cd(II), and Pd(II), were prepared. The

blue-green Cu(II) compound and the buff Pd(II) compound were anhydrous, whilst the ochre-yellow Cd(II) compound contained one mole of water. Zinc(II) chloride gave an orange compound. Repeated preparations gave reproducible analytical figures, close to the values calculated for $(ZnCl_2)_3(5\text{-}AQx)_4\ (H_2O)_4$. This formula and the very unusual strong orange-red colour suggest that coordination has occurred to both endocyclic nitrogen atoms.



I

In order to study the influence of the anion upon the structure, we also prepared compounds of 5-AQx with cobalt(II) bromide and iodide, and with cobalt(II), nickel(II), and copper(II) perchlorate. They all form compounds of type I, but some of the perchlorates could not be obtained anhydrous.

Apart from the $PdCl_2$ complex both the type I and the type II complexes are soluble in water. However, the equilibrium $Me(5\text{-}AQx)_nX_2 \rightleftharpoons MeX_2$ (solvated) + n 5-AQx is so strongly displaced to the right, that in most instances 5-AQx precipitated from aqueous solutions of the compounds immediately after the preparation. The ultraviolet spectra of the cobalt and nickel complexes in ethanol were nearly indistinguishable from the UV spectrum of 5-AQx in ethanol. This shows that extensive dissociation has occurred even in this solvent. Attempts to determine the stability constant of the $NiCl_2$ compound potentiometrically in water according to Bjerrum [7] substantiated that the formation function never exceeds 0.4.

From these results it is obvious that 5-AQx as a ligand is inferior to 8-AQ, which forms stable chelates with many of the transition metals in water and ethanol. This is consistent with the view [8] that the stability of chelates with analogous ligands often parallels their acid strength ($pK_A = 2.62$ for 5-AQx and 3.99 for 8-AQ at 25°C [9]). This conclusion derives further support from the observation that no stable inner-complexes could be prepared from the 5-AQx complexes. The $PdCl_2$ complex gave an intense blue colour with ethanolic or aqueous sodium hydroxide, but the colour faded within few seconds. The other compounds decomposed immediately to free ligand and metal hydroxide. By contrast to the corresponding violet $Pd(8\text{-}AQ)_2$,[5] the blue colour could not be extracted with chloroform. This is understandable, because only one mole of HCl can be eliminated from $Pd(5\text{-}AQx)Cl_2$. Attempts to prepare $Pd(5\text{-}AQx)_2Cl_2$ which might be able to form an inner-complex of the same type as 8-AQ were, however, unsuccessful.

The magnetic moments of three of the compounds are given in Table 1. The observed moments correspond to high-spin complexes, therefore the possibility of square-planar structures is ruled out. It is generally believed, that there is a slight difference between the moments of octahedral and tetrahedral high-spin complexes.[10] Taking this into account, the measurements

Table 1. Magnetic moments and electronic spectra of some coordination compounds of 5-aminoquinoxaline (5-AQx).

	$\mu_{eff.}$ (B.M.)	Wave number (cm^{-1})
$Fe(5\text{-}AQx)_2Cl_2$	5.4	17 900 (s) 14 000 (sh)
$Co(5\text{-}AQx)_2Cl_2$	4.7$_5$	14 600 (w) 10 000 (w)
$Ni(5\text{-}AQx)_2Cl_2$	3.0	24 000 (sh) 16 300 (w) 11 800 (w) *ca.* 8 500 (br)

indicate an octahedral structure for the nickel(II) complex. Unfortunately, both the iron(II) and the cobalt(II) complexes have borderline magnetic moments which permit no conclusions regarding their structures.

The reflectance spectra of these three compounds were plotted in the 8000—33 000 cm^{-1} region and the position of the absorption maxima are given in Table 1. The observed transitions for the nickel(II) complex strongly supports an octahedral configuration.[11] The absorptions at 8500 and 11 800 cm^{-1}, assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition, suggest some tetragonal distortion. The same behaviour has been noted for $Ni(pyridine)_4Cl_2$[12] which has been shown to have a tetragonal distorted *trans*-octahedral configuration.[13] The two weak bands at 10 000 and 14 600 cm^{-1} observed for the cobalt(II) complex agree with the assignment of an octahedral structure, whilst a tetrahedral configuration should result in a strong multicomponent band in the 12 500—16 500 cm^{-1} region.[14,15]

For the $CoCl_2$ and the $NiCl_2$ compounds, therefore, we propose the structure I. In the case of the $FeCl_2$ complex, however, the observed spectrum is complicated by a strong band at 17 900 cm^{-1}, which is probably of the charge-transfer variety, *cf.* the band at 19 000 cm^{-1} in the dipyridyl complex of Fe(II) described by Kiss and Császár.[16] A more detailed study of this complex seems necessary before an assignment of structure can be made. For the remaining compounds we consider it reasonable to assign an octahedral structure to the $CoBr_2$ and CoI_2 compounds, and a square-planar structure to the $PdCl_2$ complex.

The perchlorate complexes precipitated as di- or tetrahydrates, from which two water molecules could be easily removed to give the compounds: $Co(5\text{-}AQx)_2(ClO_4)_2 \cdot 2H_2O$, $Ni(5\text{-}AQx)_2(ClO_4)_2 \cdot 2H_2O$, and $Cu(5\text{-}AQx)_2(ClO_4)_2$. The water molecules in these compounds are tightly bound and could not be removed on drying over phosphorus(V) oxide in vacuum even at elevated temperatures. The infrared spectra showed only little splitting of the strong ν_3 and ν_4 perchlorate bands at *ca.* 1120 and 630 cm^{-1}, and the ν_1 band at *ca.* 940 cm^{-1} was only weak. A similar pattern has been found for Co(II), Ni(II), and Cu(II) perchlorate hexahydrate, where the deviation from T_d symmetry has been attributed to distortion of the perchlorate tetrahedron in the crystal lattice.[17] Therefore it is concluded, that the water molecules and not the

Table 2. Infrared N—H and C—N frequencies (cm^{-1} in KBr) of 5-aminoquinoxaline (5-AQx) and its coordination compounds.

Compound	N-H stretching	C-N stretching	NH_2 wagging
5-AQx	3448s, 3342s	1323m	—
5-AQx (0.14 M in CCl_4)	3499s, 3395s	1325m	—
5-AQx (5×10^{-2} M in benzene)	3502s, 3400s	1321m	—
$Fe(5\text{-AQx})_2Cl_2$	3213s, 3120s	1299m	1098s
$Co(5\text{-AQx})_2Cl_2$	3200s, 3116s	1299m	1105s
$Co(5\text{-AQx})_2Br_2$	3255s, 3103s 3190s 3160s	1296w	1099m
$Co(5\text{-AQx})_2I_2$	3221s, 3092s 3179s 3155s	1289w	1101s
$Co(5\text{-AQx})_2(ClO_4)_2 \cdot 2H_2O$	3283s, 3239s	1298w	*
$Ni(5\text{-AQx})_2Cl_2$	3197s, 3112s	1298w	1111m
$Ni(5\text{-AQx})_2(ClO_4)_2 \cdot 2H_2O$	3281s, 3238s	1296w	*
$Cu(5\text{-AQx})Cl_2$	3213s, 3093s 3176s, 3061s 3146s	1291w	1108m
$Cu(5\text{-AQx})_2(ClO_4)_2$	3192s, 3086s 3143s, 3060s 3040s 3016s	1292w	*
$Cd(5\text{-AQx})Cl_2 \cdot H_2O$	3213s, 3109s 3188s	1294w	1114m
$Pd(5\text{-AQx})Cl_2$	3207s, 3061m	1295w	1119m

* Masked by strong perchlorate absorptions.

perchlorate ions complete the coordination sphere. The coordination number then becomes six for Co(II) and Ni(II) and probably four for Cu(II), in agreement with the coordination number found for the compounds discussed above, where the halide ions probably are coordinated to the metal ion.

The infrared spectra of 5-AQx and the complexes in the region 400—4000 cm^{-1} are presented in Table 2 and in the experimental part.

The spectrum of 5-AQx is rather complicated, but shows similarities to that of quinoxaline [18] as well as to that of 8-AQ.[3] The monohydrate, when recorded in KBr, benzene, or chloroform, had a spectrum almost identical with that of the anhydrous compound. The reason is possibly that the water molecule is lost during the preparation of the KBr pellet or by dissolving the compound in the organic solvents. This assumption is supported by the accompanying colour change from yellow to orange.

Deuteration served to identify the bands arising from the NH_2 vibrations. The N—H stretching vibrations (NH/ND ratio 1.37) were located as two bands in the 3300—3500 cm^{-1} range, rather insensitive to changes of medium (Table 2). A similar behaviour of 8-AQ has been interpreted [2] to indicate only a small difference between the effects of inter- and intramolecular hydrogen bonding on the NH stretching vibration. In an attempt to clarify this point the molec-

ular weight of 5-AQx in benzene was determined. The value found (145 in 5×10^{-2} M solution) definitely excluded association in this solvent, leaving intramolecular hydrogen bonding or related effects as the probable reason for the small medium dependence. As expected, chelation caused the N—H stretching vibrations to shift towards lower frequencies, but a search for systematic trends was complicated by the presence of more than two peaks in this region in several of the spectra (Table 2). The NH_2 deformation vibration was mixed with the ring vibrations resulting in a strong doublet around 1600 cm^{-1}. By deuteration, the shape of these absorptions was changed, and new absorptions of medium strength appeared at *ca.* 1180 and 1075 cm^{-1}. The same holds for the complexes, of which the $NiCl_2$, the $CuCl_2$, and the $CdCl_2$ compounds have been partially deuterated. The band at 1323 cm^{-1} in 5-AQx is attributed to the C—N stretching vibration, because this band shifts to lower frequencies upon chelation (Table 2). The shift is nearly the same as found for 8 AQ [4] and α-naphthylamine,[19] where the position of this band in the free ligand is 1336 and 1287 cm^{-1}, respectively. All the complexes showed four medium to strong bands in the 1000—1100 cm^{-1} region, where the NH_2 wagging frequency is expected to occur. Only the band located in the region 1098—1119 cm^{-1} was weakened or shifted to lower frequencies upon deuteration. Therefore, this absorption is attributed at least partly to the NH_2 wagging frequency. The corresponding absorption has been found in spectra of 8-AQ chelates at 1020—1090 cm^{-1},[2] in spectra of α-naphthylamine complexes at 1025—1125 cm^{-1},[19] and in spectra of aniline complexes at 1010—1185 cm^{-1}.[20] It is interesting to note, that the observed range for this band is much smaller in the case of 5-AQx than for the three other ligands.

The eight quinoxaline ring-stretching bands expected in the 1630—1350 cm^{-1} region [18] were all observed. They were only little affected upon chelation, and no regularities in the shifts similar to those reported for pyridine [21] and quinoline [22] were found. Below 1350 cm^{-1}, the C—H in-plane and out of plane vibrations and the ring breathing vibrations [18] show very small and irregular shifts upon chelation.

EXPERIMENTAL

The analyses were carried out in the microanalysis department of this laboratory. The magnetic susceptibilities were obtained by the Gouy method. The susceptibilities were measured at two temperatures with varying field strength (5—10 Kgauss). Within the accuracy of the measurements (2—4 %) they were independent of the field strength. The results are given in Table 3. The diamagnetic corrections are taken from Foëx [23] (quinoline) and Selwood.[24] The molecular weight of 5-aminoquinoxaline was determined by the method of Neumayer.[25] The infrared spectra were obtained on a Perkin-Elmer model 337 Grating Infrared Spectrophotometer with a Hitachi Perkin-Elmer model 159 scale expander, the KBr-disc technique being used except where otherwise noted. The reflectance spectra were recorded on a Beckman DU Spectrophotometer model G 2400. Deuteration of 5-aminoquinoxaline was performed by recrystallisation from D_2O. The deuterated complexes were prepared in C_2H_5OD and/or D_2O as described for the undeuterated compounds.

5-Aminoquinoxaline monohydrate was prepared according to Jensen.[26] Recrystallisation from water and drying in the air gave long, yellow needles. By drying *in vacuo* or by heating above 60°C the compound looses water. When heated ½ h at 70°C and 1 mm Hg analytically pure *anhydrous 5-aminoquinoxaline* was obtained as small, orange crystals.[27] The m.p. is 90—91°C.

Table 3. Magnetic data of some 5-aminoquinoxaline (5-AQx) complexes.

Compound	$\chi_M \times 10^6$ 293.2°K	76.9°K	diamagn. correction $\times 10^6$	θ°	$\mu_{eff.}$ (B.M.) 293.2°K
$Fe(5\text{-}AQx)_2Cl_2$	12 010	42 320	−249	10	5.4
$Co(5\text{-}AQx)_2Cl_2$	9 310	30 550	−248	20	4.7_5
$Ni(5\text{-}AQx)_2Cl_2$	3 610	13 090	−248	10	3.0

IR-spectrum: 3448s, 3342s, *ca.* 3200 w br, 1621s, 1578m, 1550w, 1506s, 1477s, 1413w, 1394w, 1366s, 1323m, 1272w, 1239vw, 1204m, 1177w, 1135w, 1123w, 1084m, 1038m, 963vw, 911m, 878m, 861w, 830m, 754s, 585w, 547vw, 505vw, 476m, 468m, 437m.

Bis-(5-aminoquinoxaline)-iron(II) chloride. A solution of 5-aminoquinoxaline monohydrate (163 mg) in hot abs. ethanol (3 ml) was mixed in a nitrogen atmosphere with a solution of iron(II) chloride tetrahydrate (100 mg) in hot abs. ethanol (2 ml). A clear deep red solution was formed, from which the chelate began to precipitate within a few minutes. After 2 h at 5°C the solution was centrifuged and the crystals were washed with methylene chloride and dried *in vacuo*. Yield 125 mg (60 %) of small, brownish-lilac crystals, which decompose on heating at 190—195°C. (Found: C 45.70; H 3.37; Cl 16.72; N 19.91. Calc. for $C_{16}H_{14}Cl_2FeN_6$: C 46.07; H 3.38; Cl 17.00; N 20.15). A test with KSCN precluded that the unusual colour could be due to iron(III).

IR-spectrum: 3213s, 3120s, 3032w, 1615m, 1584s, 1556w, 1496s, 1479s, 1405w, 1386m, 1361s, 1299m, 1271w, 1231m, 1205m, 1160m, 1098s, 1085w, 1061s, 1046s, 1014s, 977w, 915w, 900w, 879s, 828m, 820m, 768s, 706w, 645m, 583m, 540m, 501m, 467w, 439m.

Bis-(5-aminoquinoxaline)-cobalt(II) chloride. In a nitrogen atmosphere, 5-aminoquinoxaline monohydrate (163 mg) and cobalt(II) chloride hexahydrate (119 mg) were dissolved in the minimum volume of boiling abs. ethanol (50 ml) to give a clear, dark green solution. After standing for 24 h at 5°C, the solution was centrifuged. The crystals were washed with a little abs. ethanol and dried *in vacuo*. Yield 150 mg (71 %) of pale brown rhombs, which decompose on heating at 220—225°C. (Found: C 45.70; H 3.11; Cl 16.92; Co 13.98; N 19.74. Calc. for $C_{16}H_{14}Cl_2CoN_6$: C 45.74; H 3.36; Cl 16.88; Co 14.03; N 20.00).

IR-spectrum: 3200s, 3116s, 3030w, 1617s, 1585s, 1559w, 1500s, 1480s, 1405w, 1388m, 1364s, 1299m, 1273w, 1233m, 1209m, 1161m, 1105s, 1090w, 1065s, 1053s, 1016s, 978m, 916w, 902m, 881s, 827m, 820m, 769s, 708w, 645m, 598m, 586m, 580m, 544m, 503m, 468w, 442m.

Bis-(5-aminoquinoxaline)-cobalt(II) bromide. This complex was prepared in the same way as the chloride. After standing for 3 days at 5°C the yield was 47 % of reddish-ochre cubes, which decompose on heating at about 250°C. (Found: C 37.87; H 3.11; Br 31.60; Co 11.38; N 16.36. Calc. for $C_{16}H_{14}Br_2CoN_6$: C 37.75; H 2.77; Br 31.39; Co 11.58; N 16.51).

IR-spectrum: 3255s, 3190s, 3160s, 3103s, *ca.* 3040w br, 1615m, 1586m, 1560m, 1500s, 1480s, 1408w, 1394w, 1364s, 1296w, 1262w, 1232w, 1205m, 1161m, 1099m, 1060s, 1046s, 1017s, 919m, 909m, 893m, 882m, 829m, 825m, 778s, 712vw, 647m, 590w, 582m, 570w, 522m, 502m, 439w.

Bis-(5-aminoquinoxaline)-cobalt(II) iodide. Preparation as above gave a 54 % yield of dark carmine needles, which decompose on heating at 245—250°C. (Found: C 32.08; H 2.36; Co 9.81; I 42.18; N 13.88. Calc. for $C_{16}H_{14}CoI_2N_6$: C 31.87; H 2.34; Co 9.77; I 42.09; N 13.94).

IR-spectrum: 3221s, 3179s, 3155s, 3092s, 1613m, 1584m, 1559s, 1497s, 1472s, 1401vw, 1388m, 1362s, 1289w, 1253w, 1227w, 1199m, 1149m, 1101s, 1074sh, 1061s, 1051s, 1038sh, 1018s, 979w, 917w, 877s, 827m, 821w, 772s, 711vw, 641w, 591w, 578w, 567w, 520m, 502m, 438w.

Bis-(5-aminoquinoxaline)-cobalt(II) perchlorate hydrates. The *tetrahydrate* was obtained in the same way as the cobalt chloride complex in 50 % yield. The precipitate was

dried ½ h at 25°C and 10 mm Hg. (Found: C 31.23; H 3.08; N 13.53.Calc. for $C_{16}H_{22}Cl_2CoN_6O_{12}$: C 30.98; H 3.58; N 13.55). The *dihydrate* was formed by intensive drying of the tetrahydrate (4 h at 100°C and 1 mm Hg over phosphorus(V) oxide). (Found: C 32.83; H 3.01; N 14.39. Calc. for $C_{16}H_{18}Cl_2CoN_6O_{10}$: C 32.90; H 3.11; N 14.39). Both compounds are dark olive grey; they decompose on heating, turning brown at 170—175°C and turning black at 220—225°C.

IR-spectrum of the dihydrate: 3455s, 3283s, 3239s, 3150sh, 1655m, 1617m, 1592m, 1575m, 1556m, 1502s, 1481s, 1408w, 1396m, 1369s, 1298w, 1267w, 1232m, 1209m, 1173s, 1138vs, 1121vs, 1111vs, 1099vs, 1080sh, 1065sh, 1020s, 994w, 979w, 941w, 928w, 916m, 876s, 830m, 825m, 782s, *ca.* 660w br, 638s, 628s, 596w, 586w, 531m, *ca.* 515m br, 501m, *ca.* 445w br.

Bis-(5-aminoquinoxaline)-nickel(II) chloride. 5-Aminoquinoxaline monohydrate (163 mg) and nickel(II) chloride hexahydrate (119 mg) were dissolved in boiling abs. ethanol (290 ml). After standing for 6 days at 5°C the solution was centrifuged. The crystals obtained were washed with abs. ethanol and dried *in vacuo*. Yield 137 mg (65 %) of small, yellow-olive rhombs, which decompose on heating at about 250°C. (Found: C 45.92; H 3.31; Cl 16.66; N 20.03; Ni 14.16. Calc. for $C_{16}H_{14}Cl_2N_6Ni$: C 45.76; H 3.36; Cl 16.88; N 20.01; Ni 13.98).

IR-spectrum: 3197s, 3112s, 3033w, 1622m, 1588s, 1560w, 1501s, 1483s, 1410w, 1392w, 1367s, 1298w, 1276vw, 1237w, 1211w, 1163m, 1111m, 1070s, 1056sh, 1020m, 983w, 921w, 907w, 886m, 829m, 772s, 711vw, 650w, 616w, 585w, 551m, 511w, 450w.

Bis-(5-aminoquinoxaline)-nickel(II) perchlorate hydrates. The *tetrahydrate* and the *dihydrate* were prepared in the same manner as the corresponding cobalt compounds in 55 % yield. Both hydrates are grey olive and decompose on heating at 260—265°C. (Found for the dihydrate: C 33.25; H 2.89; N 14.39. Calc. for $C_{16}H_{18}Cl_2N_6NiO_{10}$: C 32.91; H 3.11; N 14.39).

IR-spectrum of the dihydrate: 3469s, 3281s, 3238s, 1650m, 1616m, 1592m, 1574m, 1553m, 1502s, 1478s, 1406w, 1394m, 1367s, 1296w, 1264w, 1227m, 1207m, 1170s, 1139vs, 1122vs, 1110vs, 1094vs, 1080sh, 1070sh, 1020s, 993w, 977w, 940w, 926w, 917m, 873s, 829m, 825m, 782s, 638s, 629s, 596w, 546m, 516w, 506w, 447w.

5-Aminoquinoxaline-copper(II) chloride. A solution of 5-aminoquinoxaline monohydrate (163 mg) in ethanol (15 ml) was mixed with a solution of copper(II) chloride dihydrate (170 mg) in water (7.5 ml). A clear grass-green solution was formed, from which the complex started to separate almost immediately. After ½ h the solution was centrifuged and the crystals were washed with ethanol and dried *in vacuo*. Yield 165 mg (60 %) of dark blue-green needles, which decompose on heating at 185—190°C. (Found: C 34.39; H 2.65; Cl 24.92; N 15.14. Calc. for $C_8H_7Cl_2CuN_3$: C 34.36; H 2.52; Cl 25.36; N 15.03).

IR-spectrum: 3213s, 3176s, 3146s, 3093s, 3061s, 1614m, 1591m, 1559m, 1554m, 1498s, 1474s, 1403w, 1388m, 1363s, 1291w, 1258w, 1223m, 1198m, 1154m, 1108m, 1074s, 1052m, 1015s, 980w, 918m, 890m, 826m, 776s, 649w, 617w, 597w, 578w, 550m, 516w, 506m, 441w, 423w.

Bis-(5-aminoquinoxaline)-copper(II) perchlorate and dihydrate. 5-Aminoquinoxaline monohydrate (163 mg) in ethanol (8 ml) was mixed with copper(II) perchlorate hexahydrate (185 mg) in water (4 ml). Crystallisation began at once, and after 2 h the solution was centrifuged. The isolated crystals were washed with ethanol and dried ½ h at 25°C and 10 mm Hg. Yield 225 mg (80 %) of the *dihydrate*, which forms small, bluish green needles. (Found: C 32.82; H 3.25; N 14.02. Calc. for $C_{16}H_{18}Cl_2CuN_6O_{10}$: C 32.64; H 3.08; N 14.27). On heating, the compound looses water at 100—110°C to give the blue grey *anhydrous complex*. This compound decomposes on further heating at 210—215°C. (Found: C 34.61; H 2.86; N 15.23. Calc. for $C_{16}H_{14}Cl_2CuN_6O_8$: C 34.76; H 2.55; N 15.20).

IR-spectrum of the anhydrous chelate: 3192s, 3143s, 3086s, 3060s, 3040s, 3016s, 1617m, 1591m, 1566s, 1505s, 1476s, 1407w, 1397m, 1369s, 1292w, 1258w, 1225w, 1209m, 1175sh, 1142vs, 1122vs, 1109vs, 1092vs, 1070sh, 1021s, 989w, 940w, 922m, 908w, 887s, 869vw, 854w, 826m, 820w, 772s, 759w, 719vw, 638vs, 630vs, 626vs, 608m, 574m, 545m, 516w, 508m, 438w.

5-Aminoquinoxaline zinc chloride complex. 5-Aminoquinoxaline monohydrate (163 mg) in ethanol (4 ml) and zinc chloride (136 mg) in water (1 ml) were mixed to give a clear red solution. The solution was set aside at 5°C for 3 h, centrifuged, and the crystals washed with a little ethanol and dried ½ h at 25°C and 10 mm Hg. The complex (140 mg) is orange-red and on heating it turns yellow at *ca.* 120°C and white at 180°C. (Found:

C 36.49; H 3.89; Cl 19.45; N 16.01; Zn 18.74. Calc. for 4 (5-AQx)·3 $ZnCl_2$·4 H_2O: C 36.21; H 3.41; Cl 20.04; N 15.83; Zn 18.47). Repeated preparations with some variation of the relative amounts of the components gave almost identical analytical figures.

IR-spectrum: 3500sh, 3467s, 3359s, 3269s, 3211s, 3173s, 3116m, 1675m, 1616s, 1591m, 1570m, 1543w, 1514m, 1503s, 1480s, 1413w, 1393w, 1366s, 1324w, 1297w, 1277w, 1233w, 1207m, 1182w, 1160w, 1127m, 1097w, 1067m, 1050m, 1017m, 912w, 878m, 872m, 869m, 828w, 818m, 777m, 743s, 580w, 538w, 487w, 459w.

5-Aminoquinoxaline-cadmium(II) chloride monohydrate. A solution of 5-aminoquinoxaline monohydrate (163 mg) in ethanol (6 ml) was mixed with a solution of cadmium chloride (183 mg) in water (6 ml). From the clear, orange solution the complex slowly separated. After 24 h the crystals were isolated, washed with ethanol and dried ½ h at 25°C and 10 mm Hg. Yield 190 mg (55 %) of ochre yellow rhombs, which on heating turns brown-orange at *ca.* 100°C and decompose at 180—190°C. (Found: C 27.69; H 2.56; Cl 20.34; N 12.26. Calc. for $C_8H_9CdCl_2N_3O$: C 27.73; H 2.62; Cl 20.46; N 12.13). The same analysis was obtained after drying over phosphorus(V) oxide at 100°C and 1 mm Hg for 2 h.

IR-spectrum: 3513s, 3489s, 3213s, 3188s, 3109s, 3030sh, 1621m, 1591s, 1584sh, 1554w, 1495s, 1473s, 1390m, 1362s, 1294w, 1251m, 1231m, 1203m, 1157m, 1114m, 1073s, 1052m, 1022s, 992w, 908m, 865s, 831m, 821w, 779s, 719w, *ca.* 685 w br, *ca.* 590w br, 559m, *ca.* 525m br, 498m, 435m.

5-Aminoquinoxaline-palladium(II) chloride. 5-Aminoquinoxaline monohydrate (163 mg) in ethanol (12 ml) was mixed with palladium(II) chloride (178 mg) in water (8 ml). The complex, which settled at once, was filtered off, washed with ethanol and water and dried *in vacuo*. Yield 300 mg (93 %) of buff, small needles. They decompose on heating at about 250°C. (Found: C 29.61; H 2.21; Cl 21.91; N 13.08; Pd 33.05. Calc. for $C_8H_7Cl_2N_3Pd$: C 29.80; H 2.19; Cl 21.99; N 13.03; Pd 32.99).

IR-spectrum: 3207s br, 3061m, 1619m, 1594s, 1555sh, 1540s, 1498s, 1477s, 1406m, 1387m, 1370m, 1295w, 1253w, 1230m, 1195s, 1161m, 1119m, 1082s, 1054m, 1018m, 982w, 928m, 876m, 819m, 769s, 679m, 619m, 588w, 546m, 536m, 507m, 434w.

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