Oxidative dehydrogenation of diaminomaleonitrile coordinated to the nickel and platinum atoms. Synthesis and the structure of $M[HNC(CN)C(CN)NH]_2$ (M = Ni or Pt)

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The reactions of diaminomaleonitrile $H_2NC(CN)=C(CN)NH_2$ (**1**) with the nine-nuclear carboxylate nickel(II) complex $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}$ (under an inert atmosphere or in air) and with $K_2[PtX_4]$ (in air) afforded the bis-chelate mononuclear complexes $M[HNC(CN)C(CN)NH]_2$ (M = Ni (**2**) and Pt (**3**), respectively). The structural features of compounds **1**, **2**, and **3**, which were determined by X-ray diffraction analysis, are discussed.

Key words: diaminomaleonitrile, nickel and platinum complexes, synthesis, structure.

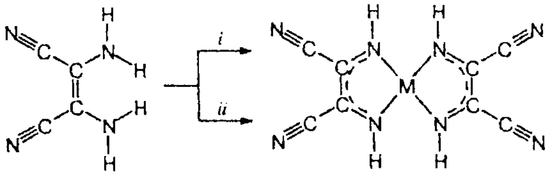
In the reactions with $K_2[MX_4]$ (M = Pd or Pt; X = Cl or NO_2) in an alkaline medium in the presence of atmospheric oxygen, *o*-phenylenediamine in platinum(II) and palladium(II) complexes readily loses hydrogen atoms to form the mononuclear bis-chelate complexes $[(RN)(NH)C_6H_4]_2M$ (M = Pt and R = H[1] or Ph[2]; M = Pd and R = Ph [2]) containing the dehydrogenated *N*-donor ligands. An analogous Ni^{II} compound, *viz.*, the complex $[(PhN)(NH)C_6H_4]_2Ni$, was synthesized by the reaction of the nine-nuclear complex $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}$ with *N*-phenyl-*o*-phenylenediamine in the presence of atmospheric oxygen.[3] It is believed that under the reaction conditions, the coordinated phenylenediamine molecule undergoes deprotonation and the resulting anionic ligand $Ar(NH)(NPh)^{2-}$ is oxidized by atmospheric oxygen to form the final complex. Within the framework of this scheme, the first stage, namely, deprotonation of the amino ligand, seems to be a necessary prerequisite for performing the overall reaction. This suggestion is confirmed by the fact that aliphatic amines that exhibit lower acidity require stronger oxidants and more harsh conditions[4] and do not enter into the reaction observed in the case of *o*-phenylenediamine.

To reveal the scope of the reaction of oxidative dehydrogenation of amines in transition-metal complexes, in this work we studied the behavior of diaminomaleonitrile (**1**) in the reaction with the nine-nuclear nickel(II) complex.

Results and Discussion

The reaction of the nine-nuclear Ni^{II} complex $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}$ with diaminomaleonitrile $H_2N(CN)C=C(CN)NH_2$ (**1**) (Ni(at) : **1** = 1 : 2) both in the presence of atmospheric oxygen and under an atmosphere of argon afforded the bis-chelate mononuclear diamagnetic complex $Ni[N(H)C(CN)C(CN)NH]_2$ (**2**) (Scheme 1).

Scheme 1



1

2: M = Ni
3: M = Pt

i. $Ni_9(HOOCCMe_3)_4(OH)_6(OOCCMe_3)_{12}$; MeCN, 80 °C;
ii. $K_2[PtX_4]$ (X = Cl, NO_2); O_2, H_2O—THF, 70—80 °C.

The presence of an alkali is not necessary for this reaction to proceed. The hydroxyl and carboxyl groups in the initial nickel complex can act as a base, abstracting the proton from the coordinated amine group. In the absence of an external oxidant of the ligand (for example, atmospheric oxygen), molecules of free compound **1** or complex **2**, which was formed in the reaction under study, can apparently act as oxidants by themselves (*i.e.*, accept electrons), because the presence of the acceptor CN groups favors the formation of radical anions, like tetracyanoethylene or tetracyanoquinodimethane. However, in the absence of atmospheric oxy-

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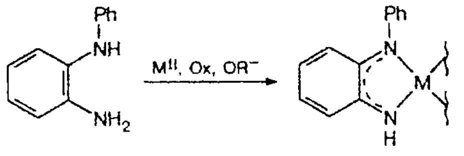
gen, the yield of bis-chelate complex **2** decreased substantially (from 40% to 20%).

We synthesized the structurally similar platinum complex of analogous composition according to a known procedure.[1,2] Unfortunately, the use of $K_2[PtX_4]$ (X = Cl or NO_2) in this case was far less efficient than in the case of preparation of *o*-phenylenediamine derivatives and we succeeded in isolating only a small amount (3—5%) of the complex $Pt[HNC(CN)C(CN)NH]_2$ (**3**). The reasons for this sharp difference in the chemical behavior of diamines are still not clearly understood. Apparently, an enhanced tendency of complex **1** (compared to *o*-phenylenediamine) to undergo polymerization and oligocondensation results in a decrease in the yield of platinum complex **3** synthesized. The yield can also be affected by redox conversions of complex **3** analogous to those observed in the reaction of $[(RN)(NH)C_6H_4]_2Pt$ with an excess of AgO_3SCF_3.[3]

Oxidation of *o*-$(NHPh)(NH_2)C_6H_4$ leads to the conversion of the phenylenediamine to the quinoid ligand, which is accompanied by a decrease in the C—N bond lengths by 0.05—0.07 Å compared to those observed in the initial diamine.[2]



The structures of complexes **2** and **3** have been established previously.[5,6] However, the crystallographic parameters of the crystals of these compounds obtained by us differ from those determined previously. It appeared that the compounds prepared by us are solvates with acetonitrile. According to the data of X-ray diffraction analysis, solvates **2** · 2MeCN and **3** · 2MeCN (Fig. 1, Tables 1 and 2) are similar in structure and contain two acetonitrile molecules of solvation per asymmetric unit (slow decomposition of **3** in the course of X-ray data collection at 22 °C is apparently due to elimination of solvate molecules). In both compounds, the M^{II} atom is bound to two HN=C—C=NH fragments (N(1)—H(1), 0.79(4) Å; N(1)—C(1), 1.331(3) Å; C(1)—C(3), 1.414(4) Å; C(3)—N(2), 1.328(3) Å (for **2**); and N(1)—C(1), 1.28(6) Å; C(1)—C(3), 1.40(5) Å; C(3)—N(2), 1.32(4) Å (for **3**)) through four nitrogen atoms. The lengths of the opposite M—N bonds in both complexes (Ni—N, 2×1.829(2) and 2×1.830(2) Å in **2**; Pt—N, 2×1.95(2) and 2×1.94(2) Å in **3**) are virtually identical. It should be noted that the C—N bonds in the five-membered metallocycles are substantially shortened compared to the standard single $C(sp^2)$—N bond (1.416 Å)[7] and are more similar to the double bond. The C—C bond length corresponds to a shortened single bond (the standard values of the $C(sp^2)$—$C(sp^2)$ and $C(sp^2)$=$C(sp^2)$ bond lengths are 1.460 and 1.317—

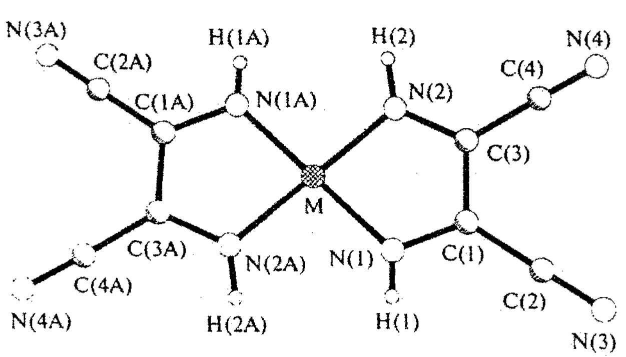


Fig. 1. Structures of the complexes $M[N(H)C(CN)C(CN)NH]_2$ (M = Ni (**2**) or Pt (**3**)).

Table 1. Bond lengths (*d*) and bond angles (ω) in complex **2** · 2 MeCN

Bond	d/Å	Angle	ω/deg
Ni(1)—N(1)	1.830(2)	N(1)—Ni(1)—N(2)	84.7(1)
Ni(1)—N(1A)	1.830(2)	N(2)—Ni(1)—N(1A)	95.3(1)
N(1)—H(1)	0.797(49)	N(2)—Ni(1)—N(2A)	180.0(1)
N(2)—C(3)	1.328(3)	Ni(1)—N(1)—C(1)	114.7(2)
N(4)—C(4)	1.140(4)	N(1)—C(1)—C(2)	124.5(2)
C(1)—C(2)	1.423(4)	C(2)—C(1)—C(3)	122.9(2)
C(3)—C(4)	1.439(3)	N(2)—C(3)—C(1)	113.9(2)
C(5)—H(53)	0.947(50)	C(1)—C(3)—C(4)	122.7(2)
C(5)—H(51)	0.570(53)	N(5)—C(6)—C(5)	178.4(4)
Ni(1)—N(2)	1.829(2)	N(1)—Ni(1)—N(1A)	180.0(1)
Ni(1)—N(2A)	1.829(2)	N(1)—Ni(1)—N(2A)	95.3(1)
N(1)—C(1)	1.331(3)	N(1A)—Ni(1)—N(2A)	84.7(1)
N(3)—C(2)	1.152(4)	Ni(1)—N(2)—C(3)	114.1(2)
N(5)—C(6)	1.132(5)	N(1)—C(1)—C(3)	112.7(2)
C(1)—C(3)	1.414(4)	N(3)—C(2)—C(1)	179.2(2)
C(5)—C(6)	1.443(6)	N(2)—C(3)—C(4)	123.5(2)
C(5)—H(52)	0.910(47)	N(4)—C(4)—C(3)	178.7(3)

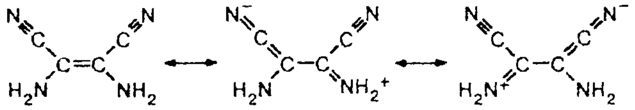
Table 2. Bond lengths (*d*) and bond angles (ω) in molecule **3** · 2 MeCN

Bond	d/Å	Angle	ω/deg
Pt(1)—N(1)	1.952(22)	N(1)—Pt(1)—N(2)	79.1(12)
Pt(1)—N(1A)	1.952(22)	N(2)—Pt(1)—N(1A)	100.9(12)
N(1)—C(1)	1.280(64)	N(2)—Pt(1)—N(2A)	180.0(1)
N(3)—C(2)	1.165(43)	Pt(1)—N(1)—C(1)	116.2(21)
C(1)—C(3)	1.402(53)	N(1)—C(1)—C(3)	114.9(30)
C(3)—C(4)	1.495(71)	C(2)—C(1)—C(3)	121.6(45)
C(1S)—C(2S)	1.541(98)	N(2)—C(3)—C(4)	122.2(34)
Pt(1)—N(2)	1.940(35)	N(3)—C(2)—C(1)	173.6(58)
Pt(1)—N(2A)	1.940(35)	N(1S)—C(1S)—C(2S)	169.9(67)
N(2)—C(3)	1.323(37)	N(1)—Pt(1)—N(1A)	180.0(1)
N(4)—C(4)	1.133(67)	N(1)—Pt(1)—N(2A)	100.9(12)
C(1)—C(2)	1.441(48)	N(1A)—Pt(1)—N(2A)	79.1(12)
N(1S)—C(1S)	1.078(72)	Pt(1)—N(2)—C(3)	115.3(26)
		N(1)—C(1)—C(2)	123.4(39)
		N(2)—C(3)—C(1)	113.6(37)
		C(1)—C(3)—C(4)	122.4(34)
		N(4)—C(4)—C(3)	174.0(49)

1.331 Å, respectively).[7,8] It should be noted that similar values of the M—N (1.827(4) and 1.957(8) Å for the Ni- and Pt-containing bis-chelate complexes, respectively), C=N (1.330(4) and 1.323(13) Å), and C—C (1.403(5) and 1.416(19) Å) bond lengths were observed in the structures of the nonsolvated complex $Ni[HNC(CN)C(CN)NH]_2$ [5] and the cocrystallizate $Pt[HNC(CN)C(CN)NH]_2 \cdot Pt(PhCN)_2Cl_2$ [6] studied previously.

The structure of ligand **1** can be represented as a combination of resonance structures **1a** and **1b** (Scheme 2).

Scheme 2



1a **1b** **1b**

When considering the structures of the ligands in complexes **2** and **3**, it is appropriate to compare their structural characteristics with the structural data on the free ligand[9] rather than with the average interatomic distances in the isolated C=N and C=C bonds. According to our data, the virtually planar diaminomaleonitrile moiety (Fig. 2, Table 3) contains C—N and C=C bonds whose lengths are close to the standard values (N(1)—C(1), 1.373(2) Å; C(1)—C(3), 1.353(2) Å; C(3)—N(2), 1.393(2) Å), unlike the above-mentioned distances (C—N and C—C) observed in the dehydrogenated and coordinated ligands in complexes **2** and **3**. The C≡N bond lengths are equal in all three molecules (Tables 1—3). Therefore, the conversion of diaminomaleonitrile into the planar "semidiimine" ligand, which is bidentate-coordinated to the Ni^{II} and Pt^{II} atoms, leads to a change in the electron density distribution in the resulting five-membered metallocycles but does not affect the C≡N groups. The IR spectra of complexes **2** and **3** have typical stretching vibration bands of the C≡N (at 2210 and 2198 cm^{-1} (**2**) and 2200 cm^{-1} (**3**)) and N—H bonds (3275 and 3228 cm^{-1} (**2**) and 3210 and 3160 cm^{-1} (**3**)). Noteworthy also are the substantially shortened M—N bonds in electron-deficient 16-electron complexes **2** and **3** compared to the sum of the covalent radii of these atoms, which is apparently indicative of additional interactions between the electron pairs of the nitrogen atoms and the unoccupied orbitals of the nickel and platinum atoms.

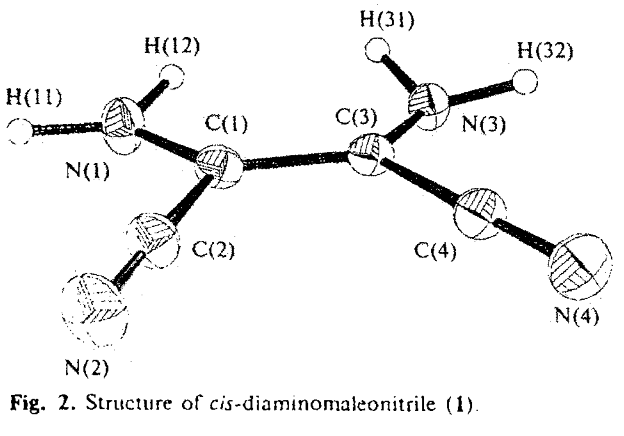


Fig. 2. Structure of *cis*-diaminomaleonitrile (**1**).

Table 3. Bond lengths (*d*) and bond angles (ω) in) molecule **1**

Bond	*d*/Å	Angle	ω/deg
N(1)—C(1)	1.373(2)	N(1)—C(1)—C(2)	117.6(1)
N(3)—C(3)	1.393(2)	C(2)—C(1)—C(3)	117.9(1)
C(1)—C(2)	1.439(2)	N(3)—C(3)—C(1)	124.0(1)
C(3)—C(4)	1.429(2)	C(1)—C(3)—C(4)	118.7(1)
N(2)—C(2)	1.142(2)	N(1)—C(1)—C(3)	124.5(1)
N(4)—C(4)	1.142(2)	N(2)—C(2)—C(1)	179.2(2)
C(1)—C(3)	1.353(2)	N(3)—C(3)—C(4)	117.1(1)
		N(4)—C(4)—C(3)	179.6(2)

The resulting compounds **2** and **3** contain C≡N groups, which are potentially able to coordinate the metal atom, and electron-rich five-membered metallocycles, in which the electron density is essentially delocalized. Due to these factors as well as to the formal presence of the unoccupied and occupied orbitals of the metal atoms, these compounds are promising donor ligands in the chemical assembly of heterometallic clusters. Note that recently we have demonstrated that the Pt-containing complex $[(PhN)(NH)C_6H_4]_2Pt$ can be used as a building block for preparing the heterobimetallic derivative $(OC)Pt[\mu\text{-}N,N\text{-}C_6H_4(N)(NPh)]_2ReCl[(NH)(NPh)C_6H_4]$.[10]

In conclusion, note that all amines that undergo oxidative dehydrogenation are characterized by higher acidity of the N—H bond compared to amines of the aliphatic series (ethylenediamine, 1,2-cyclohexanediamine, *etc.*), which are inert in this reaction. Apparently, the ability of the amine to undergo deprotonation is a necessary prerequisite for the reaction under study.

Experimental

All operations associated with the synthesis of the complexes were performed with the use of anhydrous solvents both in air and under an inert atmosphere (if necessary). The IR spectra of the compounds were recorded on a Specord M82 instrument (as KBr pellets).

Synthesis of the complex $Ni[HNC(CN)C(CN)NH]_2$ (2). A solution of diaminomaleonitrile (**1**) (0.204 g, 1.89 mmol) in MeCN (10 mL) was added to a solution of $Ni_9(HOOCCMe_3)_4(\mu_4\text{-}OH)_3(\mu_3\text{-}OH)_3(\mu_n\text{-}OOCCMe_3)_{12}$ (1 g, 0.42 mmol) in MeCN (30 mL). The reaction mixture was boiled for 30 min and then slowly cooled to ~20 °C on an oil bath. The resulting needle-like bronze-green crystals were separated from the mother liquor by decantation, washed with cold MeCN, and dried *in vacuo*. The yield was 52 mg (0.19 mmol, 20% with respect to the initial **1**). Storage of the

Table 4. Crystallographic parameters of ligand **1** and complexes **2** and **3**

Parameter	**1**	**2**	**3**
Formula	$C_8H_8N_8$	$C_{12}H_8N_{10}Ni$	$C_{12}H_8N_{10}Pt$
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a/Å	5.800(2)	4.289(2)	4.625(2)
b/Å	18.290(6)	7.327(3)	7.174(2)
c/Å	5.207(2)	13.259(5)	13.244(3)
α/deg		99.10(3)	97.44(3)
β/deg	108.19(2)	96.41(3)	97.41(3)
γ/deg		103.96(3)	105.62(3)
V/Å^3	524.8(3)	394.3(3)	413.4(2)
Z	4	1	1
ρ_{calc}/g cm^{-3}	1.368	1.245	1.933
Radiation, λ/Å	Mo-Kα 0.71073	Mo-Kα 0.71073	Mo-Kα 0.71073
θ-2θ scanning range/deg	2—52	2—54	3—56
Number of measured reflections	1099	2168	2076
Number of reflections with $I > 4\sigma$	885	1742	1118
Weighting scheme,	$w^{-1} = \sigma^2(F) + kF^2$		
k	0.0026	0.0013	0.0374
R	0.042	0.041	0.108
R_w	0.068	0.052	0.147

Table 5. Atomic coordinates (×10^4) and equivalent isotropic thermal parameters (U_{eq}×10^3/Å^2) in the structure of **2** · 2 MeCN

Atom	x	y	z	U_{eq}
Ni(1)	0	0.5	0.5	27(1)
N(1)	1790(5)	2970(3)	4982(2)	30(1)
N(2)	−161(5)	4491(3)	3596(1)	31(1)
N(3)	4622(6)	−712(3)	3689(2)	42(1)
N(4)	1037(7)	1774(4)	1327(2)	54(1)
N(5)	7224(8)	6189(5)	1912(2)	65(1)
C(1)	2113(5)	2139(3)	4045(2)	29(1)
C(2)	3480(6)	556(3)	3845(2)	32(1)
C(3)	970(5)	3012(3)	3254(2)	30(1)
C(4)	1017(7)	2341(4)	2177(2)	38(1)
C(5)	4126(11)	7714(7)	648(3)	54(1)
C(6)	5847(7)	6871(4)	1366(2)	42(1)
H(1)	2571(102)	2536(64)	5431(34)	72(13)
H(2)	−938(103)	5183(72)	3175(42)	86(15)
H(51)	5084(117)	8066(75)	423(41)	74(19)
H(52)	2100(126)	6932(70)	399(37)	88(16)
H(53)	3057(108)	8497(64)	1041(36)	70(12)

Table 6. Atomic coordinates (×10^4) and their equivalent isotropic thermal parameters (U_{eq}×10^3/Å^2) in the structure of **3** · 2 MeCN

Atom	x	y	z	U_{eq}
Pt(1)	1/2	0	0	73(1)
N(1)	5068(100)	591(28)	1485(15)	94(16)
N(2)	2950(92)	2031(30)	65(15)	122(15)
N(3)	3945(82)	3206(53)	3725(20)	78(15)
N(4)	221(128)	5648(41)	1329(23)	111(20)
C(1)	3959(147)	1978(49)	1790(20)	109(24)
C(2)	3804(140)	2589(52)	2857(25)	89(21)
C(3)	2947(129)	2909(37)	1006(21)	97(20)
C(4)	1271(133)	4399(37)	1197(22)	100(20)
N(1S)	−2605(61)	−1485(81)	3043(33)	100(24)
C(1S)	−1264(168)	−2020(58)	3602(25)	115(27)
C(2S)	1092(170)	−2690(97)	4283(42)	116(31)
H(2A)	1937	2340	−486	80

Table 7. Atomic coordinates (×10^4) and their equivalent isotropic thermal parameters (U_{eq}×10^3/Å^2) in the structure of **1**

Atom	x	y	z	U_{eq}/Å^2
N(1)	980(2)	5898(1)	4436(3)	54(1)
N(2)	6798(2)	5378(1)	8041(3)	66(1)
N(3)	378(2)	7007(1)	8180(2)	42(1)
N(4)	5960(2)	6795(1)	12973(3)	61(1)
C(1)	2695(2)	6056(1)	6862(3)	40(1)
C(2)	4974(2)	5674(1)	7515(3)	48(1)
C(3)	2414(2)	6562(1)	8638(2)	37(1)
C(4)	4387(2)	6693(1)	11044(3)	43(1)
H(11)	1229(33)	5522(11)	3297(35)	59(4)
H(12)	−626(40)	6147(12)	4187(40)	65(5)
H(31)	−1010(36)	6834(10)	7100(43)	63(5)
H(32)	276(30)	7223(10)	9765(38)	51(4)

resulting green reaction solution in air at ~20 °C resulted in an increase in the yield to 40%. Found (%): C, 35.4; H, 1.0; N, 41.5. $C_8H_2N_8Ni$. Calculated (%): C, 35.42; H, 1.48; N, 41.33. IR (KBr, ν/cm^{-1}): 3275 m, 3228 m, 2210 m, 2198 m, 1428 s, 1355 m, 1302 w, 1200 w, 1090 w, 1034 w, 1000 w, 766 s, 740 w, 634 w, 516 m.

Synthesis of the complex Pt[HNC(CN)C(CN)NH]$_2$ (3). *A.* Water (5—10 mL) was added to a suspension of $K_2[Pt(NO_2)_4]$ (1.251 g, 2.74 mmol) in boiling MeCN (20 mL) until the complex was completely dissolved. Compound **1** (0.590 g, 5.48 mmol) was added to the reaction solution. The mixture was boiled for 1 h. The resulting green solution was cooled to ~20 °C and bronze-green needle-like crystals that precipitated were separated from the solution be decantation, washed with cold MeCN, and dried *in vacuo.* The yield was 57 mg (0.14 mmol, 5%).

B. A mixture of $K_2(PtCl_4)$ (0.98 g, 2.35 mmol) and complex **1** (0.51 g, 4.66 mmol) was ground in a mortar in air in the presence of Et_3N (3 mL) and THF (2 mL). After removal of Et_3N and THF, the dark-blue product that formed was dissolved in THF (50 mL) and applied to a chromatography column (Kieselgel 60, 60—230 mesh, 3×20 cm, hexane), and the blue zone was eluted with a 1 : 1 THF—hexane mixture. The blue eluate was concentrated to dryness, and the finely crystalline precipitate that formed was washed with ether from unconsumed diaminomaleonitrile and dried *in vacuo.* The yield was 59 mg (0.143 mmol, 6%). Found (%): C, 23.4; H, 0.2; N, 27.8. $C_8H_2N_8Pt$. Calculated (%): C, 23.59; H, 0.98;

N, 27.52. IR (KBr, ν/cm^{-1}): 3400 s, 3328 s, 3210 m, 3160 s, 2200 s, 1640 m, 1614 s, 1365 s, 1320 m, 1246 m, 722 m, 626 m, 524 m, 466 w.

X-ray diffraction study. Single crystals of $H_2N(CN)C=C(CN)NH_2$ (**1**) were prepared by slow evaporation of the solution of the commercial reactant (Fluka) in ether. Single crystals of complex **2** · 2MeCN were grown by keeping a solution of **2** in MeCN at 0 °C for 48 h. Single crystals of **3** · 2MeCN suitable for X-ray diffraction analysis were prepared by slow cooling of a hot acetonitrile solution of the complex to −20 °C for 3 h on an oil bath. In all the cases, the crystals were glued to glass needles using rapidly solidifying epoxy resin in air and transferred to a diffractometer. The experimental X-ray data sets (θ-2θ scanning technique) were collected on an automated four-circle Siemens R3m/v diffractometer (at −20 °C for **1** and **3** and at −112 °C for **2**). The unit cell parameters were determined and refined using 24 equivalent reflections with $2\theta < 24$—28°. In all the cases, three strong reflections with $0 < \chi < 60°$ were used as standards. The standard reflections revealed no significant intensity variation in the course of data collection for **1** and **2** and, therefore, no corrections were applied. The crystal of complex **3** decomposed in the course of data collection and, therefore, the standard corrections were applied; however, no qualitative improvement of the X-ray diffraction data set was achieved. The structures were solved by direct methods, which revealed the positions of all nonhydrogen atoms. These atoms were then refined with anisotropic thermal parameters. The positions of the hydrogen atoms in molecules **1** and **2** were located from the difference Fourier syntheses and refined isotropically. The positions of the hydrogen atoms in the structure of **3** were calculated geometrically. Absorption correction for compound **3** was applied at the stage of isotropic refinement using a standard program.[11] All calculations were carried out using the SHELXTL PLUS program package (PC version).[12] The crystallographic parameters of the compounds under study and selected details of the refinement are given in Table 4. The principal geometric characteristics of the molecules are listed in Tables 1—3. The atomic coordinates are given in Tables 5—7.

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