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Synthesis and Safety Properties of New Explosive Coordination Compounds

Andrzej Wojewódka,[1*] Janusz Bełzowski [2]

[1] *Silesian University of Technology, Faculty of Chemistry, 7 Strzody St., 44-100 Gliwice, Poland*
[2] *Mesko S.A., Pionki, Poland*
[*] *E-mail: Andrzej.Wojewodka@polsl.pl*

Abstract: The present paper details the synthesis of new explosive complexes of the DDT type and the investigation of their sensitiveness to friction and impact. Fourteen new compounds, specifically nitrate and perchlorate complexes of various transition block metals with 5-(2,4,6-trinitrophenylamino)tetrazole, commonly called picrylaminotetrazole (PAT), were synthesised. The nitrate complexes were obtained in yields varying between 8.1% and 75.1%, whereas the perchlorate complexes had yields between 24.9% and 67.3%, with yields typically near the upper bound of the given ranges for both classes of complexes and the low yields obtained for $[Co(PAT)_3](NO_3)_3$ and $[Cd(PAT)_3](ClO_4)_3$ being the exception rather than the rule. The structures of these compounds were unambiguously established via XRF and IR spectroscopy, as well as via elemental analysis. Detailed analyses of the safety properties of these new materials were performed in terms of their sensitiveness to friction and impact. In general, the obtained compounds present relatively low sensitivity to mechanical stimuli, like friction and impact, with the nitrate complexes of Ni and Zn exhibiting high sensitivity to impact (1-2 Nm). The rest of the investigated compounds show low sensitivity to mechanical stimuli, comparable to classical blasting materials like PETN, RDX or HMX. It should be noted that, in general, the nitrates were more sensitive to mechanical stimuli than their perchlorate analogues.

Keywords: transition metal complexes, 5-picrylaminotetrazole, explosives, safety properties

1 Introduction

Even 70-80 years ago, explosives were perceived to be only nitro compounds or alcohol nitrates. Compounds like azides or fulminates were not straightforwardly called explosives, but compounds able to explode, and were used as primary explosives in detonation or ignition caps. Mercury fulminate, lead azide or tetrazene show high sensitivity to mechanical stimuli, such as friction and impact, and consequently their use poses a huge risk for humans and industrial installations [1, 2].

The first reports on the potential application of transition metals coordination compounds as explosives, especially as primary explosives, appeared in the late fifties and early sixties of the previous century. However, due to the extremely high sensitivity of such compounds to mechanical stimuli, research in this field was discontinued. A renewed interest in these derivatives was observed in the eighties, as new explosives like NHN [tris(hydrazine)nickel(II) nitrate(V)] and HATP [di(3-hydrazino-4-amino-1,2,3-triazole)copper(II) perchlorate] were developed [3-5]. Studies in this area continue to this day and have yielded a new generation of these compounds, exhibiting low sensitivity to mechanical stimuli, high energetic parameters [6, 7] and susceptibility to stimulation by laser light. These materials can be used as a base in blasting or ignition caps initiated by a laser beam [8, 9].

In this article, we report on the synthesis of several perchlorate and nitrate metal complexes with 5-picrylaminotetrazole (PAT) as a ligand and the results of testing their basic safety properties – sensitivity to friction and impact. These compounds are potentially new explosives, with possibly broad application in laser and conventional igniters, caps or detonators. All of the tested compounds were detonated by a 200 mg lead azide charge, in standard aluminium cylindrical capsules with an internal diameter of 6.4 mm.

2 Experimental and Results

2.1 Materials and methods

2.1.1 General synthesis

Synthesis of the final transition metal complexes was carried out in two stages. In the first stage, picrylaminotetrazole [5-(2,4,6-trinitrophenylamino)tetrazole] was obtained by reacting 5-aminotetrazole with picryl chloride (1-chloro-2,4,6-trinitrobenzene) in boiling ethanol [10], as shown in Figure 1.

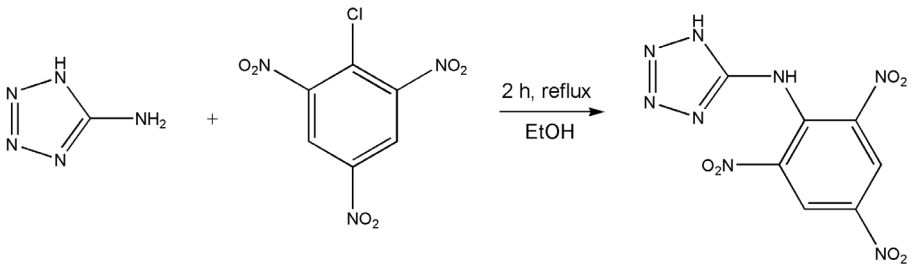

Figure 1. Reaction scheme for the synthesis of 5-(2,4,6-trinitrophenylamino) tetrazole (PAT)

The second stage involved the preparation of the target complexes. An aqueous solution of the appropriate metal nitrate or perchlorate was stirred in the presence of PAT at 60 °C for 6 h (Figure 2). Commercially available metal nitrate salts were used for the synthesis of the nitrate complexes. The synthesis of perchlorate complexes involved the appropriate metal perchlorates, which were obtained by precipitating their respective carbonates from a solution of the corresponding nitrate and their subsequent reaction with chloric(VII) acid (70% aq. solution, Aldrich, Cat. No. 380083). In these reactions, PAT was used in excess (10% with respect to the inorganic salts). The obtained products were filtered off from the post-reaction mixtures and recrystallized from ethanol, in order to remove free PAT, utilising the higher solubility of PAT in ethanol. The yields of the expected products were in the range of 8.1-75.1%, as listed in Table 1, along with the amounts of the reactants used.

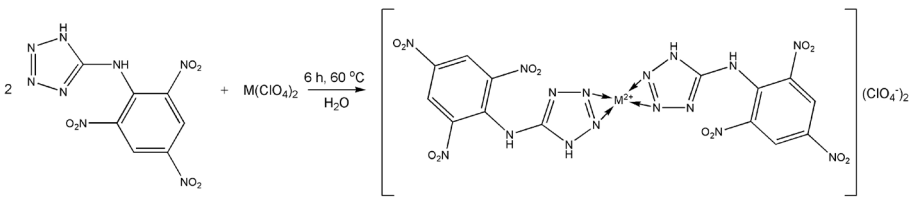

Figure 2. Scheme for obtaining PAT complexes

Elemental analyses of C, H, N, were performed using a Perkin Elmer Series II CHNS/O Analyzer 2400; IR spectra in the solid phase (KBr pellet) were recorded on a BioRad FTIR 175S spectrometer, in the 640-4000 cm^{-1} range; metal content analyses were performed via X-Ray Fluorescence (XRF), using an EDXRF Spectro Xepos apparatus.

2.1.2 Determination of sensitiveness to friction

The compounds were tested for their sensitivity to friction on a Peters apparatus using the methodology included in [11], based on the Polish equivalent PN-EN 13631-3:2006.

2.1.3 Determination of sensitiveness to impact

Sensitivity to impact of the compounds was tested on a Kast impact apparatus, using 1 kg and 5 kg hammers, according to the methodology outlined in [12], based on the Polish equivalent PN-EN 13631-4:2004.

2.2 Synthetic procedures

2.2.1 5-(2,4,6-Trinitrophenylamino)tetrazole (PAT, $C_7H_4N_8O_6$)

Ethanol (200 mL) and picryl chloride (41.79 g, Aldrich, Cat. No. 79874) were added to a flask equipped with a reflux condenser and the resulting suspension was heated to boiling. When the solid phase had dissolved, 5-aminotetrazole (14.36 g, Aldrich, Cat. No. 550728) was added in small portions over the course of 30 min. The mixture was then heated on a water bath for 2.5 h. The reaction mixture was concentrated on a rotary evaporator to half of its initial volume and cooled to room temperature. The obtained precipitate was filtered off on a Büchner funnel. The recovered solid was recrystallized from ethanol. Final product mass: 35.00 g (70.0% yield). The results of the spectral analyses of the product are summarised in Table 2.

2.2.2 Nitrate analogues – $[M(PAT)_n](NO_3)_m$

PAT was added in portions (44 mmol or 66 mmol) over the course of 30 min to an aqueous solution of the appropriate nitrate(V) (100 mL, containing 20 mmol or 30 mmol respectively). The mixture was then heated to 60 °C and stirred magnetically for 6 h. The mixture was cooled to room temperature and the precipitate was filtered off on a Büchner funnel. The solid was recrystallized from ethanol.

The masses, yields and the analytical summary are presented in Tables 1 and 2.

2.2.3 Perchlorate analogues – $[M(PAT)_n](ClO_4)_m$

PAT was added in portions (44 mmol or 66 mmol) over the course of 30 min to an aqueous solution of the appropriate perchlorate prepared from nitrate(V) (100 mL, containing 20 mmol or 30 mmol respectively). The mixture was then

heated to 60 °C and stirred magnetically for 6 h. The mixture was cooled to room temperature and the precipitate was filtered off on a Büchner funnel. The solid was recrystallized from ethanol.

The masses, yields and the analytical summary are presented in Tables 1 and 2.

2.2.4 Analytical characteristics

The masses of the reactants used in the syntheses and the yields of the obtained products are given in Table 1.

Table 1. Masses of reactants used, obtained products and yields

Compound formula	Reactants			Product	
	Type of salt (Sigma-Aldrich Cat. No.)	Mass of metal nitrate(V)/ chlorate(VII) [g]	Mass of PAT [g]	Mass of product [g]	Yield [%]
$[Cu(PAT)_2](NO_3)_2$	$Cu(NO_3)_2 \cdot 2.5H_2O$ (31288)	4.65	13.03	6.73	40.8
$[Ni(PAT)_3](NO_3)_2$	$Ni(NO_3)_2 \cdot 6H_2O$ (72252)	5.82	19.55	12.67	53.7
$[Hg(PAT)_2](NO_3)_2$	$Hg(NO_3)_2 \cdot H_2O$ (230421)	6.85	13.03	14.04	75.1
$[Co(PAT)_3](NO_3)_3$	$Co(NO_3)_2 \cdot 6H_2O$ (239267)	5.82	19.55	1.91	8.1
$[Cr(PAT)_3](NO_3)_3$	$Cr(NO_3)_3 \cdot 9H_2O$ (239259)	8.00	19.55	7.04	27.3
$[Zn(PAT)_3](NO_3)_2$	$Zn(NO_3)_2 \cdot 6H_2O$ (228737)	5.95	19.55	11.67	49.2
$[Cd(PAT)_3](NO_3)_2$	$Cd(NO_3)_2 \cdot 4H_2O$ (20911)	6.17	19.55	15,20	63.5
$[Cu(PAT)_2](ClO_4)_2$	$Cu(ClO_4)_2$ [a]	5.25	13.03	10.04	58.7
$[Ni(PAT)_3](ClO_4)_2$	$Ni(ClO_4)_2$ [a]	5.15	19.55	7.24	31.6
$[Hg(PAT)_2](ClO_4)_2$	$Hg(ClO_4)_2$ [a]	7.99	13.03	13.25	66.8
$[Co(PAT)_3](ClO_4)_3$	$Co(ClO_4)_2$ [a]	5.16	19.55	8.44	36.8
$[Cr(PAT)_3](ClO_4)_3$	$Cr(ClO_4)_3$ [a]	7.01	19.55	13.88	56.0
$[Zn(PAT)_3](ClO_4)_2$	$Zn(ClO_4)_2$ [a]	4.42	19.55	15.51	67.3
$[Cd(PAT)_3](ClO_4)_2$	$Cd(ClO_4)_2$ [a]	6.23	19.55	5.98	24.9

[a] The metal perchlorate was prepared from the corresponding nitrate, the Sigma-Aldrich catalogue number of which is listed in the table.

Table 2. Results of elemental, XRF and IR analyses of the obtained compounds

Compound formula	Elemental analysis/XRF		Summary of FTIR spectroscopic data [cm^{-1}]			
	Calculated [%]	Found [%]	NO_3^- / ClO_4^-	Tetrazole ring	Amine bridge	Picryl ring
PAT	C 28.39, H 1.36, N 37.84	C 28.31, H 1.41, N 37.80	-	1466 1267, 1157, 1079, 1044, 920, 755, 742	1639, 1700	1604, 1540, 1338, 1060, 926, 718, 648
$[Cu(PAT)_2](NO_3)_2$	Cu 8.15, C 21.56, H 1.03, N 32.33	Cu 8.01, C 21.50, H 0.99, N 32.16	1624, 1423, 1301, 819	1624, 1089, 919	1697	1624, 1423, 1301, 819
$[Ni(PAT)_3](NO_3)_2$	Ni 5.48, C 23.55, H 1.13, N 34.00	Ni 5.51, C 23.48, H 1.11, N 33.89	1623, 1422, 1297, 818	1623, 1084, 925	1695	1623, 1422, 1297, 818
$[Hg(PAT)_2](NO_3)_2$	Hg 21.88, C 18.34, H 0.88, N 27.50	Hg 21.90, C 18.26, H 0.86, N 27.59	1624, 1425, 1298, 817	1624, 1085, 924	1691	1624, 1425, 1298, 817
$[Co(PAT)_3](NO_3)_3$	Co 5.20, C 22.25, H 1.07, N 33.37	Co 5.30, C 22.21, H 1.11, N 33.42	1622, 1422, 1295, 816	1622, 1086, 924	1695	1622, 1422, 1295, 816
$[Cr(PAT)_3](NO_3)_3$	Cr 4.62, C 22.39, H 1.07, N 33.57	Cr 4.71, C 22.30, H 1.01, N 33.63	1621, 1426, 1296, 815	1621, 1084, 925	1691	1621, 1426, 1296, 815
$[Zn(PAT)_3](NO_3)_2$	Zn 6.07, C 23.40, H 1.12, N 33.79	Zn 6.01, C 23.29, H 1.13, N 33.72	1623, 1420, 1301, 815	1623, 1084, 921	1691	1623, 1420, 1301, 815
$[Cd(PAT)_3](NO_3)_2$	Cd 9.99, C 22.42, H 1.08, N 32.37	Cd 9.90, C 22.38, H 1.10, N 32.46	1622, 1421, 1296, 813	1622, 1084, 921	1692	1622, 1421, 1296, 813
$[Cu(PAT)_2](ClO_4)_2$	Cu 7.43, C 19.67, H 0.94, N 26.22	Cu 7.30, C 19.57, H 0.86, N 26.14	1056	1538, 1087, 915	1680	1621, 1425, 1298, 1147, 1046
$[Ni(PAT)_3](ClO_4)_2$	Ni 5.12, C 22.01, H 1.06, N 29.33	Ni 5.03, C 21.90, H 1.00, N 29.19	1056	1543, 1089, 920	1682	1625, 1426, 1301, 1149, 1043
$[Hg(PAT)_2](ClO_4)_2$	Hg 20.22, C 16.95, H 0.81, N 22.60	Hg 20.11, C 16.81, H 0.80, N 22.42	1058	1539, 1089, 915	1682	1621, 1425, 1297, 1149, 1042
$[Co(PAT)_3](ClO_4)_3$	Co 4.73, C 20.25, H 0.97, N 26.98	Co 4.81, C 20.12, H 0.90, N 26.91	1061	1542, 1085, 916	1682	1625, 1422, 1295, 1148, 1046
$[Cr(PAT)_3](ClO_4)_3$	Cr 4.20, C 20.36, H 0.98, N 27.14	Cr 4.26, C 20.42, H 1.01, N 27.16	1060	1544, 1088, 915	1680	1622, 1426, 1297, 1148, 1042
$[Zn(PAT)_3](ClO_4)_2$	Zn 5.67, C 21.88, H 1.05, N 29.16	Zn 5.73, C 21.96, H 1.04, N 29.22	1061	1542, 1088, 920	1680	1623, 1425, 1295, 1143, 1042
$[Cd(PAT)_3](ClO_4)_2$	Cd 9.37, C 21.02, H 1.01, N 28.02	Cd 9.31, C 21.13, H 1.06, N 28.00	1061	1540, 1086, 920	1681	1624, 1422, 1301, 1143, 1043

Table 2 shows the chemical characteristics of the complexes – elemental and spectroscopic analyses. The FTIR spectra recorded for PAT and $[Cd(PAT)_3](NO_3)_2$ are shown in Figures 3a and 3b, respectively.

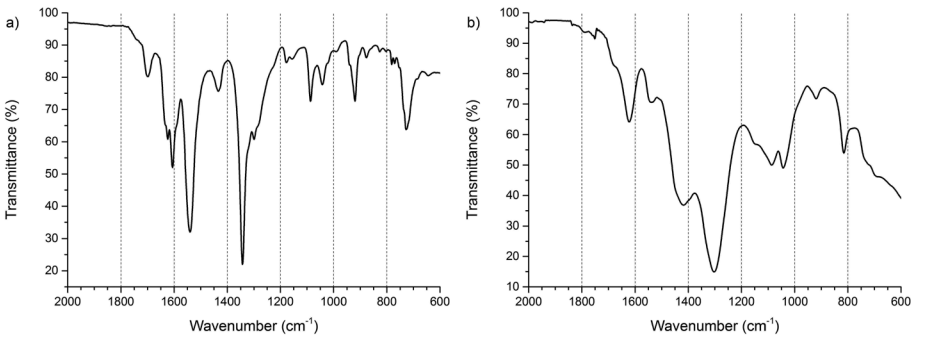

Figure 3. Sample FTIR spectra of (a) PAT; (b) $[Cd(PAT)_3](NO_3)_2$

2.3 Sensitivity to mechanical stimuli

For each compound, the maximum friction insufficient for generating an explosive reaction in all six tests and the minimum friction generating an explosive reaction in at least one of the six tests, were determined. Similarly, the maximum and minimum impact energies were determined using Kast's apparatus.

2.3.1 Friction sensitivity

The sensitivities to friction of the obtained compounds are presented in Table 3.

Among the investigated compounds, the chlorate(VII) copper(II) complex (42-48 N), as well as the corresponding nitrate (28-30 N), $[Hg(PAT)_2](NO_3)_2$ (24-28 N) and also $[Ni(PAT)_3](ClO_4)_2$ (42-48 N) were the ones most sensitive to friction. Conversely, significant resistance to this mechanical stimulus was observed for the nitrate complexes of zinc (192-216 N) and cobalt (144-166 N), and the perchlorates of chromium (168-180 N) and cobalt (144-160 N). With respect to PETN – a reference explosive – the nitrate complexes of nickel, chromium, cadmium, cobalt and zinc were significantly less sensitive to friction. In the case of the perchlorates, high friction resistance was observed for cadmium, zinc, cobalt and chromium complexes.

2.3.2 Impact sensitivity

The impact sensitivities of the obtained compounds are given in Table 3.

Table 3. Summary of friction and impact sensitivity parameters for the investigated complexes

Compound	Sensitivity to friction [N]	Sensitivity to impact [Nm]
$[Cu(PAT)_2](NO_3)_2$	30	4
$[Hg(PAT)_2](NO_3)_2$	80	20
$[Co(PAT)_3](NO_3)_3$	160	4
$[Ni(PAT)_3](NO_3)_2$	48	2
$[Zn(PAT)_3](NO_3)_2$	128	3
$[Cd(PAT)_3](NO_3)_2$	128	7.5
$[Cr(PAT)_3](NO_3)_3$	180	4
$[Cu(PAT)_2](ClO_4)_2$	48	25
$[Hg(PAT)_2](ClO_4)_2$	28	>25
$[Co(PAT)_3](ClO_4)_3$	160	15
$[Ni(PAT)_3](ClO_4)_2$	112	7.5
$[Zn(PAT)_3](ClO_4)_2$	216	4
$[Cd(PAT)_3](ClO_4)_2$	128	10
$[Cr(PAT)_3](ClO_4)_3$	112	>25

The compounds most sensitive to impact (1-2 Nm) are the nitrate(V) complexes of nickel and zinc. Relatively stable complexes, under these conditions were: $[Hg(PAT)_2](NO_3)_2$ – 15 Nm, $[Co(PAT)_3](ClO_4)_3$ – 10 Nm, $[Cu(PAT)_2](ClO_4)_2$ – 20 Nm, $[Hg(PAT)_2](ClO_4)_2$ – 25 Nm and $[Cr(PAT)_3](ClO_4)_3$ – 25 Nm. In comparison with pentrite, the nitrate complexes of cadmium and mercury are less sensitive to impact, as are practically all of the perchlorates.

3 Conclusions

(1) The synthesis of 14 hitherto unknown, transition metal complexes was performed. Elemental, IR and XRF spectral analyses confirmed the structures of the obtained complexes; these compounds were generally isolated in good yields, with the exception of $[Co(PAT)_3](NO_3)_3$.

(2) The obtained compounds, in general, exhibited relatively low sensitivity to mechanical stimuli, such as friction and impact. The only two compounds to deviate from this were $[Ni(PAT)_3](NO_3)_2$ and $[Zn(PAT)_3](NO_3)_2$, whose sensitivity to impact was 1-3 Nm. The remaining tested compounds showed low sensitivity to mechanical stimuli, on the level of classical blasting materials like PETN, RDX or HMX [13] and higher than other complexes,

similar to explosives like NHN or its cobalt analogue (CoHN) [6].

(3) It should be noted that the nitrates were, in general, more sensitive to mechanical stimuli than their perchlorate analogues.

(4) The perchlorate complexes of chromium and cadmium were noted for their good resistance to both mechanical stimuli.

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References

[1] Huynh, M. H. V.; Hiskey, M. A.; Meyer, T. J.; Wetzler, M. Green Primaries: Environmentally Friendly Energetic Complexes. *PNAS* **2006**, *103*: 5409-5412.

[2] Sinditskii, V. P.; Fogelzang, A. E. Energetic Materials Based on Co-ordination Compounds. *Russ. J. Chem.* **1997**, *41*(4): 74-80.

[3] Zhu, S. G.; Wu, Y. C.; Zhang, W. Y.; Mu, J. G. Evaluation of a New Primary Explosive: Nickel Hydrazine Nitrate (NHN) Complex. *Propellants Explos. Pyrotech.* **1997**, *12*: 317-320.

[4] Chernai, A. V.; Sobolev, V. V.; Chernai, V. A.; Ilyushin, M. A.; Dlugashek, A. Laser Ignition of Explosive Composition Based on Di(3-hydrazino-4-amino-1,2,3-triazole)-Copper(II) Prechlorate. *Combust., Explos. Shock Waves (Engl. Transl.)* **2003**, *39*(3): 335-339.

[5] Chhabra, J. S.; Talawar, M. B.; Makashir, P. S.; Asthana, S. N.; Singh, H. Synthesis, Characterization and Thermal Studies of (Ni/Co) Metal Salts of Hydrazine: Potential Initiatory Compounds. *J. Hazard. Mater.* **2003**, *99*: 225-239.

[6] Cudziło, S.; Nita, M. Synthesis and Explosive Properties of Copper(II) Chlorate(VII) Coordination Polymer with 4-Amino-1,2,4-triazole Bridging Ligand. *J. Hazard. Mater.* **2010**, *177*: 146-149.

[7] Wojewódka, A.; Bełzowski, J.; Wilk, Z.; Staś, J. Energetic Characteristics of Transition Metal Complexes. *J. Hazard. Mater.* **2009**, *171*: 1175-1177.

[8] Cudziło, S.; Szmigielski, R. Synthesis and Investigation of Some Di-(R-1,2,4-triazolato)copper(II) Perchlorates. *Biuletyn WAT* **2000**, *12*: 5-17.

[9] Wojewódka, A.; Bełzowski, J.; Romanowski, M.; Kudła, S. Pyrotechnic Mixture Ignited by Low Power Laser Light. *6th Int. Conf. IPOEX, Explosives: Research – Application – Safety*, Ustroń, Poland **2009**, *23*.

[10] Agrawal, J. P.; Bapat, V. K.; Surve, R. N. Synthesis, Characterization and Evaluation of Explosive Properties of 5-Picrylamino-1,2,3,4-Tetrazole. *High Energy Materials Conference and Exhibits, IIT, 2nd*, Madras **1998**, *403*.

[11] *Explosives for Civil Uses. High Explosives*. Part 3: *Determination of Sensitiveness to Friction of Explosives*. European Standard EN 13631-3, **2004**.

[12] *Explosives for Civil Uses. High Explosives*. Part 4: *Determination of Sensitiveness to Impact of Explosives*. European Standard EN 13631-4, **2002**.
[13] Meyer, R.; Köhler, J.; Homburg, A. *Explosives*. 6th ed., Wiley-VCH, Weinheim **2007**; ISBN 978-3-527-31656-4.